THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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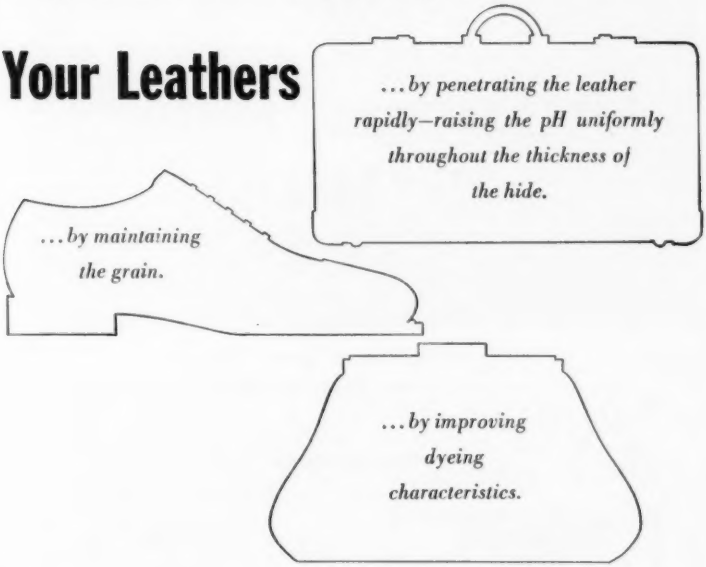
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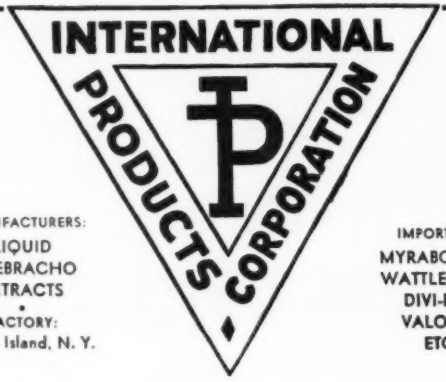

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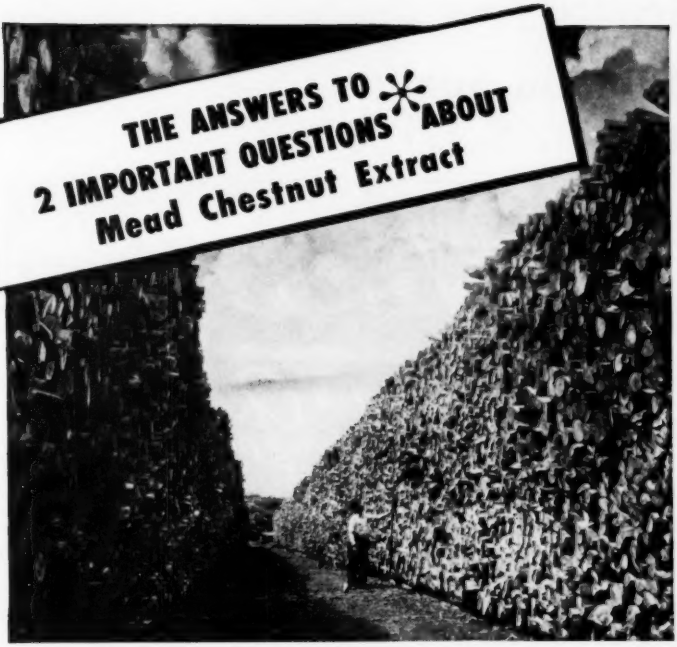

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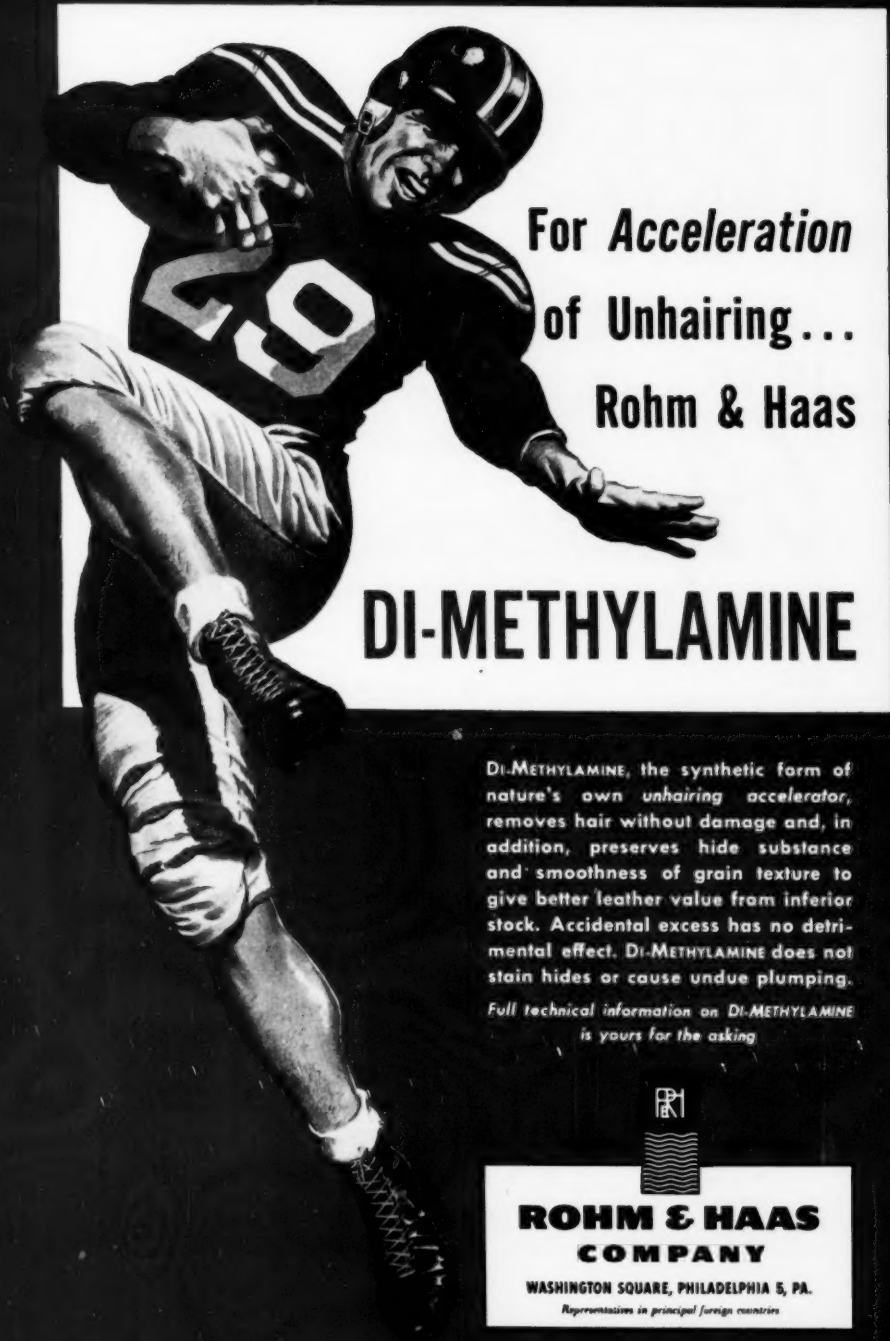

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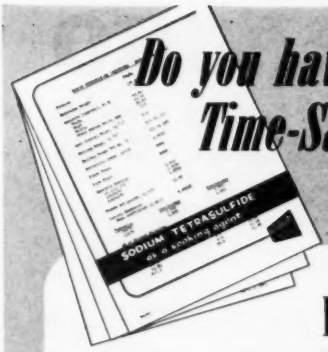

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SECRETARY'S NOTICE

Regarding the International Union of Leather Chemists Societies, 1953 Meeting at Barcelona, Spain

The following letter has been received from Mr. A. Harvey, Honorary General Secretary of the International Union of Leather Chemists Societies.

INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

"Craigieburn"
Duppas Hill Rd.,
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Surrey.
21st. August, 1952

Dr. Fred O'Flaherty
Dept. of Leather Research,
University of Cincinnati,
Cincinnati, Ohio.
United States of America.

Dear Dr. O'Flaherty,

I have pleasure in informing you that the 1953 biennial Conference of Leather Trades' Chemists will be held in Barcelona, Spain, by invitation of the Spanish Association of Leather Trades' Chemists from Sept. 13th to Sept. 18th inclusive.

Further details will be issued from time to time.

Yours sincerely,

A. Harvey,

Hon. General Secretary.

Dr. H. G. Turley, who is a delegate to the above meeting, requests any member desirous of submitting or presenting a paper at the foregoing meeting should advise him at once of such intention.

Zirconium Tannage

VI. ANALYSIS OF LEATHERS CONTAINING ZIRCONIUM*

By I. C. SOMERVILLE and J. WENDKOS

Contribution from the
Research Laboratories of the Rohm and Haas Company
Philadelphia, Pa.

INTRODUCTION

It is now over twenty years since we first discovered how to apply zirconium salts on a tannery scale in making satisfactory leather.[1] In the past ten years many millions of square feet have been produced having zirconium as the sole or principal tanning agent. During this period we have had a number of inquiries about the best method of analyzing leather for zirconium, and have supplied details of our preferred procedure to several tanners and to Government and commercial laboratories. Some time ago the Committee on Mineral Tannage asked us to publish a standard method which could serve as a basis for consideration as an Official Method of the Association. We plan to outline at this time the general procedure, and indicate how far the methods can be relied on to cover all the mineral constituents frequently present in some leathers. At the outset I should like to say that the actual analyses were carried out entirely by my colleague, Mr. Wendkos, who has worked in our Leather Laboratory for many years under Dr. Turley's general direction. The observations which he made in the course of following standard methods have enabled him to devise improvements, some of which are reported in this paper.

ESTIMATION OF ZIRCONIUM SALTS IN AQUEOUS SOLUTION

The first step in the analysis of leathers containing zirconium and other mineral constituents is to ash, fuse, and so obtain these salts in water soluble form. The details of this procedure will be given later.

Zirconium alone : ZrO_2

In order to establish the accuracy of the proposed methods a number of solutions were made up containing known amounts of zirconium, titanium, aluminum, chrome, iron, and silica. A stock zirconium solution was made up by dissolving 70 grams re-crystallized zirconium oxychloride and diluting to 750 ml.

The ZrO_2 was determined in two ways:

(a) by precipitation with ammonia	4.01 grams per 100 ml. stock solution	
(b) by precipitation with p.hydroxyphenyl-arsonic acid	4.03 grams	" "
Calculated from $ZrOCl_2.6H_2O$	4.01 grams	" "

*Presented at the 48th Annual Meeting, Swampscott, Mass., June 3, 1952.

The ammonia precipitation was carried out in about the usual manner for aluminum.[2] 100 ml. of stock solution was diluted to 1 liter (Solution D). A 50 ml. aliquot was diluted with approximately 50 ml. water, acidified with a small amount of hydrochloric acid, then heated to boiling and the flame removed. Concentrated ammonium hydroxide was added dropwise till the solution was slightly alkaline (to Brom Thymol Blue as internal indicator), then the precipitate allowed to settle for 5 minutes, and filtered through ashless paper (Whatman No. 40), washed with hot water till free from chlorides, dried and ignited in a weighed platinum dish to constant weight.

The precipitation with p.hydroxyphenylarsonic acid was carried out according to the method described by Simpson and Chandlee.[3] A 25 ml. aliquot of Solution D was diluted with approximately 75 ml. water, acidified with 12–15 ml. concentrated hydrochloric acid, then heated to boiling. 25 ml. of a 4 per cent aqueous solution of p. hydroxyphenylarsonic acid was added, and the solution boiled gently for about 10 minutes, then allowed to cool to room temperature. The precipitate was filtered through ashless paper, washed thoroughly with a solution of dilute hydrochloric acid (0.25 N) containing 0.5 per cent reagent, dried, and ignited to ZrO_2 in a porcelain crucible to constant weight. This operation was carried out in a fume hood using a Fisher burner. A platinum dish cannot be used in this ignition since it is attacked by the arsenic present. In some cases it is difficult to complete the ignition in porcelain and it may be simpler to utilize a muffle furnace around 1000°C. if available.

These two methods have proved very satisfactory in our experience, but many other reagents have been suggested for the determination of zirconium.

These include:

Gravimetric:	Ammonium phosphate	:	Lundell & Knowles, *J.A.C.S.* **41**, 1806 (1919)
	Selenious acid	:	Smith & James, *J.A.C.S.* **42**, 1764 (1920)
	Mandelic acid	:	Kumins, *Ind. Eng. Chem. An. Ed.* **19**, 376 (1947)
	p.-Brommandelic acid	:	Hahn, *Anal. Chem.* **23**, 1260(1951)
Colorimetric:	Chloranilic acid	:	Thamer & Voight, *J.A.C.S.* **73**, 3201 (1951)

Zirconium alone : Acid

A characteristic of all zirconium salts is their strong tendency to hydrolyze in aqueous solution. This is utilized in the determination of acidity following the procedure recommended in the Official Methods for chrome salts, C-1. It is essential to use a dilute solution and boil long enough to effect complete hydrolysis. Actually it is easier to observe the end point than with chrome

liquors since the precipitate formed is white. A typical procedure was as follows:

> 25 ml. of a 2 per cent solution of $ZrOCl_2.6H_2O$ were diluted with 600 ml. water in a 10 inch porcelain dish, 0.5 ml. of 1 per cent solution of phenolphthalein added, and heated to boiling. While boiling gently, 35.0 ml. 0.1 *N* NaOH were added until a faint pink color persisted for 5 minutes. Since 1 ml. of 0.1 *N* sodium hydroxide is equivalent to 0.00365 g. HCl (0.0049 g. H_2SO_4), total acid as HCl = 35 X 0.00365 g. = 0.1278 g. HCl. Hence
>
> Acid as HCl present in $ZrOCl_2.6H_2O$ = 25.55 per cent.

Zirconium alone : Basicity

The basicity is expressed according to Schorlemmer's system:

$$\text{Per Cent Basicity} = \frac{(\text{Total } ZrO_2 - ZrO_2 \text{ comb. with acid})}{\text{Total } ZrO_2} \times 100$$

As an example, the figures obtained above showed:

Total ZrO_2 present in $ZrOCl_2.6H_2O$	43.0%
Acid as HCl present in $ZrOCl_2.6H_2O$	25.55%

Since $ZrO_2 + 4\ HCl \rightleftarrows ZrCl_4 + 2\ H_2O$

4 X 36.5 (146 g.) HCl are equivalent to 123 g. ZrO_2

Hence 25.55 g. HCl are equivalent to 21.5 g. ZrO_2

Substituting above,

$$\text{Basicity} = \frac{(43.0 - 21.5)}{43.0} \times 100 = 50.0\%$$

Mixtures of Zirconium with other salts

Known amounts of each of the other salts mentioned earlier were added one at a time to 100 ml. portions of the stock zirconium oxychloride solution, diluted to volume, and aliquots taken to determine ZrO_2 and the other metal present.

Zirconium plus titanium

A solution of titanium potassium oxalate was made up to contain 1.00 per cent TiO_2. 100 ml. of this solution was mixed with 100 ml. of zirconium stock solution, acidified with hydrochloric acid and diluted to 1 liter.

Precipitation was carried out as above on 50 ml. aliquots using (a) ammonia, (b) p.hydroxyphenylarsonic acid, to yield $ZrO_2 + TiO_2$. The latter was then determined colorimetrically on another aliquot. In the method as described by Simpson and Chandlee[3] zirconium alone can be precipitated in strongly acid solution using a large excess of hydrogen peroxide which holds titanium in solution. It is difficult, however, to determine titanium in the filtrate. Our preferred method, therefore, is to precipitate both metals together and determine TiO_2 colorimetrically using titanium potassium oxalate as standard then find ZrO_2 by difference. The results came out as in Table 1.

TABLE 1

		Found	Calc.
$ZrO_2 + TiO_2$	(a)	4.97 grams	5.01 grams
	(b)	4.93	5.01
TiO_2		1.00	1.00
ZrO_2 (by diff.)	(a)	3.97	4.01

Hence both methods show reasonably good agreement for zirconium and titanium.

Zirconium plus aluminum

A solution of aluminum sulfate was made up to contain 1.06 per cent Al_2O_3. 100 ml. of this solution was mixed with 100 ml. of zirconium stock solution, acidified with hydrochloric acid and diluted to 1 liter.

Precipitation was carried out as above on 50 ml. aliquots using

(a) ammonia, to yield $ZrO_2 + Al_2O_3$
(b) p.hydroxyphenylarsonic acid, to yield ZrO_2 alone

The results came out as in Table 2.

TABLE 2

		Found	Calc.
$ZrO_2 + Al_2O_3$	(a)	5.15 grams	5.07 grams
ZrO_2	(b)	4.03	4.01
Al_2O_3 (by diff.)		1.12	1.06

Hence zirconium can be determined accurately in presence of aluminum using method (b). In this test the Al_2O_3 figure was high, though reduced from 1.19 by re-precipitation.

Zirconium plus chrome

In fusing leathers containing chrome the latter is obtained in the form of chromate. A solution of sodium bichromate was made up to contain the equivalent of 4 per cent Cr_2O_3. 100 ml. of this solution was mixed with 100 ml. of zirconium stock solution, acidified with hydrochloric acid and diluted to 1 liter.

Precipitation was carried out as above on 50 ml. aliquots using

(a) ammonia, to yield ZrO_2
(b) p.hydroxyphenylarsonic acid, to yield ZrO_2

Chrome was determined volumetrically on another aliquot. The results came out as in Table 3.

TABLE 3

		Found	Calc
ZrO_2	(a)	4.16 grams	4.01 grams
	(b)	4.03	4.01
Cr_2O_3		4.01	4.00

Hence zirconium can be determined accurately in presence of chrome using method (b), without upsetting the chrome determination. The ZrO_2 using method (a) was lowered from 4.25 to 4.16 grams by double precipitation, but some chrome was still present as evidenced by a greenish color on ignition.

Zirconium plus iron

Iron is not normally present in zirconium leathers except in small amount—at least not in white leathers. A solution of ferrous ammonium sulfate was, therefore, made up to contain only 0.04 per cent Fe_2O_3. 100 ml. of this solution was mixed with 100 ml. of zirconium oxychloride stock solution, acidified with hydrochloric acid, and diluted to 1 liter.

Precipitation was carried out as above on 50 ml. aliquots using

(a) ammonia, to yield $ZrO_2 + Fe_2O_3$
(b) p.hydroxyphenylarsonic acid, to yield ZrO_2

Fe_2O_3 was determined colorimetrically on another aliquot. The results came out as in Table 4.

TABLE 4

		Found	Calc.
$ZrO_2 + Fe_2O_3$	(a)	4.03 grams	4.05 grams
Fe_2O_3 colorimetrically		0.039	0.04
ZrO_2 (by diff.)		3.99	4.01
ZrO_2	(b)	4.00	4.01

Hence zirconium and iron can be determined accurately in this way.

Zirconium plus silica

Silica is most frequently present in zirconium leather from the use of clay given as filler, in which case it is also accompanied by aluminum. For this experiment, however, the aluminum was omitted and a grade of sodium silicate selected which was not precipitated by acid but was thrown out by ammonia. A solution of $Na_2SiO_3.9H_2O$ was prepared to contain 1.00 per cent SiO_2. 100 ml. of this solution was mixed with 100 ml. of zirconium stock solution, acidified with hydrochloric acid and diluted to 1 liter.

Precipitation was carried out as above using

(a) ammonia, to yield $ZrO_2 + SiO_2$
(b) p hydroxyphenylarsonic acid, to yield ZrO_2

SiO_2 was determined by fuming off the ignited residue from (a) by heating with hydrofluoric acid plus sulfuric acid. The results came out as in Table 5.

TABLE 5

		Found	Calc.
$ZrO_2 + SiO_2$	(a)	5.04 grams	5.01 grams
SiO_2 (fuming with HF)		1.03	1.00
ZrO_2 (residue)		4.01	4.01
ZrO_2	(b)	3.99	4.01

Hence zirconium and silica can be determined accurately in this way.

Zirconium plus aluminum plus silica

In order to check the effect obtained with both silica and aluminum present, 100 ml. of the same solution of sodium silicate was mixed with 100 ml. of the solution of aluminum sulfate mentioned above, 100 ml. of zirconium stock solution added, acidified with hydrochloric acid and the whole diluted to 1 liter.

Precipitation was carried out as above using

(a) ammonia, to yield $ZrO_2 + SiO_2 + Al_2O_3$
(b) p hydroxyphenylarsonic acid, to yield ZrO_2

SiO_2 was determined by fuming the ignited oxides from (a) with hydrofluoric acid plus sulfuric acid; Al_2O_3 was found by difference between the residue and the figure for ZrO_2 from (b). The results came out as in Table 6.

TABLE 6

		Found	Calc.
$ZrO_2 + SiO_2 + Al_2O_3$	(a)	6.14 grams	6.07 grams
SiO_2 (fuming with HF)		1.11	1.00
$ZrO_2 + Al_2O_3$ (residue)		5.04	5.07
ZrO_2	(b)	3.98	4.01
Al_2O_3 (by diff.)		1.06	1.06

These figures show good agreement for zirconium and aluminum; in this test the silica was high.

The general conclusion from this series of experiments is that the methods suggested can be utilized in the determination of zirconium in conjunction

with these other metals. The figures obtained are, we believe, sufficiently accurate for tannery control purposes, and the procedures can be carried out in a straightforward way with equipment normally available in a leather laboratory.

General Procedure for Leathers Containing Zirconium

In the analysis of leathers containing zirconium the procedure as regards sampling and preparation of sample for analysis follows exactly that described in the Official Methods for vegetable or chrome leathers, D-1. Determinations of

Moisture
Total Ash
Petroleum Ether Extract
Nitrogen
Hide Substance
Sulfates
Basicity

follow in the same way as for Chrome Tanned Leathers, D-1 to D-4. When only zirconium is present, the Basicity can be calculated as outlined above for zirconium salts. When other minerals such as chrome or titanium are present it is usually not possible to apportion the available acid to specific oxides, unless zirconium is the only tanning agent and the others are known to be present as fillers.

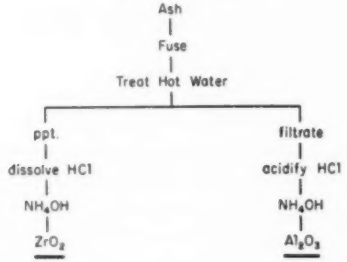
Mineral Constituents

The Ash is fused so as to obtain all minerals present in a water soluble form, then these are determined as outlined above. The present Official Methods for chrome utilize a wet fusion of the Ash with perchloric acid, (which is ineffective with ignited ZrO_2) or reaction with perchloric acid following careful wet oxidation of the leather sample. The latter method could probably be worked out for zirconium leathers, but in all our experiments to date we have utilized dry fusion of the Ash. When this problem was first investigated the Official Methods for chrome called for fusion with a mixture of equal parts of sodium carbonate, potassium carbonate and borax glass. In our early work we found that the resulting fusion mixture seemed to dissolve more readily when hydrated borax was substituted for the anhydrous borax glass. This observation simplifies the method considerably.

The former Official Methods called for dissolving the fusion mixture in hot water and acidifying with hydrochloric acid and a few drops of sulfuric acid. When only zirconium is present this procedure is satisfactory—the zirconium salt remains in solution which is diluted to volume and an aliquot used to determine ZrO_2 as described above. When other minerals are present along with zirconium we have found that the carbonate fusion can be modified

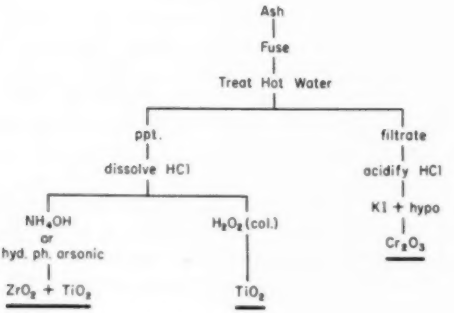
to secure more effective separation of individual components. After treating the alkaline fusion mixture with hot water as usual, the solution is filtered and the filtrate (augmented with washings from the insolubles) then acidified with hydrochloric acid, diluted to volume and aliquots used to determine metals present. The insolubles (washed free of alkali) are dissolved in 4 *N* hydrochloric acid, diluted to volume, and aliquots used to determine metals present. For example, if aluminum and zirconium are the only components at the end of fusion the aluminum is present as soluble sodium aluminate, the zirconium as insoluble zirconium hydroxide. The separation is illustrated in Figure 1.

FIGURE 1



A similar advantage to this procedure shows up when chrome is present at the same time as zirconium and titanium. This can occur, for example, when a pale bluish-white leather is tanned using a blend of zirconium and chrome, then given titanium oxide as filler. In this case, when the alkaline fusion is taken up in hot water the chrome is soluble as chromate while the zirconium and titanium remain in the insolubles and can be dissolved in acid and determined as before. A typical separation is shown in Figure 2.

FIGURE 2



These examples illustrate how this modification of the carbonate fusion method can provide more effective separation of individual components.

However, we should like to point out at this time that an alternative method is available for determination of titanium in presence of chromate. The carbonate fusion is acidified directly with hydrochloric acid and diluted to volume. Aliquots are used to determine chrome volumetrically, ZrO_2 plus TiO_2 gravimetrically with ammonia or p.hydroxyphenylarsonic acid, and titanium colorimetrically. Even in presence of chromate the latter is feasible since the blue coloration formed by hydrogen peroxide with chromate is fugitive. At the dilution employed the color due to chrome in the solution practically disappears, so that the yellow color due to the titanium present can be readily matched with the color standard. This effect of peroxide on chromate is noted in Treadwell and Hall [4] and in Prescott and Johnson, [5] but so far as we know has not been applied previously to the colorimetric determination of titanium in presence of chromate.

Typical Leather Analysis

These methods were applied to two commercial leathers:

A. Black kid suede tanned with zirconium and chrome.
B. White kid suede tanned with zirconium alone but given clay and titanium oxide as filler.

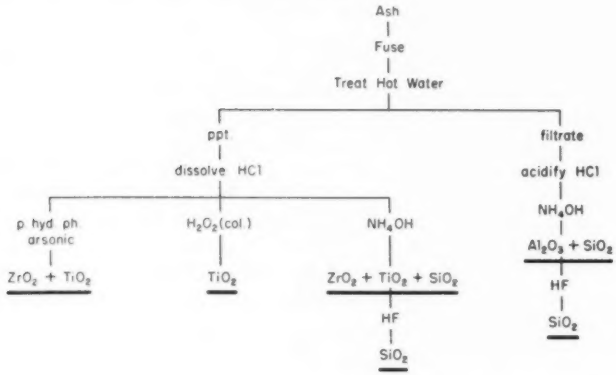
The procedure used in A. was the same as that shown in Figure 2 except that no titanium was present. The results are given in Table 7.

TABLE 7

Moisture	9.7%
Total Ash	15.0
Petroleum Ether Extract (Extracted leather showed pH 3.6)	1.4
Nitrogen	11.6
Hide Substance	65.3
On Hide Substance Basis	
Sulfates—Combined (as SO_3)	2.6
—Neutral (as SO_3)	0.0
ZrO_2	7.2
Cr_2O_3	8.9

The procedure used in B. was a little more complicated as is illustrated in Figure 3.

FIGURE 3



Here the method was expanded to take care of the silica present. This was volatilized from the precipitate of Combined Oxides by treatment with hydrofluoric acid in presence of sulfuric acid. Note that some silica is present in the original precipitate as well as in the filtrate—these fractions must be added together to give the correct value. The results are shown in Table 8.

TABLE 8

Moisture	8.6%
Total Ash	22.2
Petroleum Ether Extract	6.6
(Extracted leather showed pH 3.5)	
Nitrogen	9.4
Hide Substance	53.0
On Hide Substance Basis	
Sulfates—Combined (as SO_3)	9.1%
—Neutral (as SO_3)	0.0
ZrO_2	20.2
TiO_2	6.8
Al_2O_3	0.6
SiO_2	2.4
Basicity	65.0
Interpretation	
Tannage	20.2% ZrO_2
Filler	6.8% TiO_2
Filler	3.0% clay

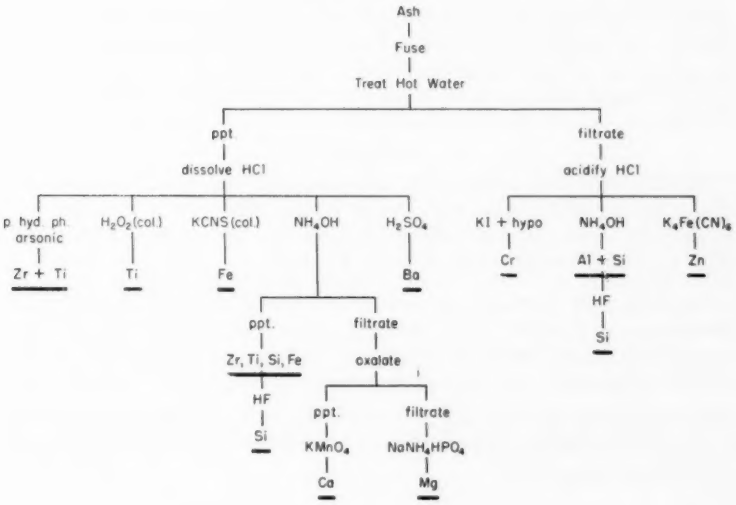
Comprehensive Method

The methods described above and illustrated by application to these two leathers cover the mineral constituents most commonly met with in commercial zirconium leathers today. We have extended these in an exploratory way to see how far they are applicable to a still wider range of ten metals which might conceivably be present in white leather. For instance, these might be introduced as shown below:

From Tannage	From Filler	Metals Present
zirconium	——	Zr
chrome	——	Cr
alum	clay	Al, Si
——	titanium oxide	Ti
——	lithopone	Ba, Zn
——	talc	Mg, Si
iron	——	Fe
——	chalk	Ca

A mixture was prepared by grinding together these tanning materials and fillers in proportions which might possibly represent those utilized in making leather. The materials were analyzed individually at the start, then the same methods applied to the composite. The procedure is simply an expansion of those described above, and is illustrated in Figure 4.

FIGURE 4



The procedure for Zr, Ti, Fe, Si, Cr and Al was exactly as before. In the solution from 'insolubles', Ca was precipitated in the filtrate from the Combined Oxides by adding oxalate; and Mg from this secondary filtrate by adding Microcosmic Salt; Ba was precipitated as sulfate. From the original 'solubles' Zn was determined volumetrically with ferrocyanide.

The results are shown in Table 9.

TABLE 9

Ingredients				Calculated in Composite	Found in Composite
30 parts zirconium salt showing		34.6%	ZrO_2	17.3%	18.0%
8 parts chrome salt	"	21.0	Cr_2O_3	2.8	3.6
6 parts Titanox AWD	"	80.0	TiO_2	8.1	8.6
		14.6	Al_2O_3	4.6	2.7
5 parts clay	"	36.9	Al_2O_3		
		49.9	SiO_2	7.7	6.9
3 parts talc	"	55.3	SiO_2		
		27.0	MgO	1.6	1.7
5 parts lithopone	"	46.3	BaO	3.9	3.8
		6.0	ZnO	0.5	0.5
3 parts chalk	"	60.1	CaO	3.1	3.9
iron (impurities)			Fe_2O_3	0.2	0.2

Considering the complexity of this mixture the results though by no means perfect are encouraging, and this approach could be explored further to advantage. Actually it is very seldom that white leather will contain all these ingredients at the same time and short cuts can be made when qualitative tests show some minerals to be absent.

Summary

Methods have been outlined for the estimation of zirconium salts in solution, alone and in conjunction with other mineral salts. These are sufficiently accurate for tannery control purposes and can be readily carried out in equipment available in the average leather laboratory.

These methods have been applied to the analysis of leathers containing zirconium, and are illustrated by results found for a black suede kidskin tanned with zirconium plus chrome, and for a white suede kidskin tanned with zirconium alone using titanium oxide and clay as fillers.

An exploratory approach has been made to see how far they can form the basis for a comprehensive method applicable to leather containing ten possible mineral ingredients.

References

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38, 326 (1943)
43, 345 (1948)
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2. A.L.C.A. Methods D-3, G-26
3. Simpson and Chandlee, *Ind. Eng. Chem. An. Ed.* **10,** 642 (1938)
4. Treadwell and Hall, Analytical Chemistry Volume 1, p. 147 (Sixth Edition, 1927)
5. Prescott and Johnson, Qualitative Chemical Analysis, p. 153 (Seventh Edition, 1917)

Received June 26, 1952.

Discussion

Dr. Ludwig Seligsberger: I think, the merit of Dr. Somerville's paper is that for the first time he recognizes the complexities of analysis which today confront some of our laboratories, particularly in connection with white leather. It is interesting to see what happens to a leather, as we have seen it right now, with twelve or fourteen constituents, when we subject it to the fusion method as outlined by Dr. Somerville.

The fusion method has found no place so far in our Methods Book. The Methods Book advocates wet oxidation and it is obvious that fusion is superior to it. Anybody who has worked with wet oxidation on such leathers will find that you have almost everything in solution except the barium sulfate and maybe part of the titanium oxide and of the clay. You can never say what you have in the leather as a metallic tanning agent and what you have as a filler. The fusion method is superior because it separates a few substances in an easy manner. It separates perfectly the chrome as chromate from the iron and brings about the separation of zinc and alum from barium and calcium.

The problem, which Dr. Somerville mentioned, of getting a reliable figure for alum confronted me and probably everybody who worked along these lines.

I have found that it is highly desirable to separate fillers and tanning agents more completely, and I feel that the best way to accomplish this is to use dilute sulfuric acid or an organic acid on the leather first, which will dissolve, of course, the leather and bring all the tanning agents in solution. All the fillers and pigments except the zinc will remain behind. Clay and titanium are unaffected by sulfuric acid and, of course, zirconium will be in solution together with the chrome and the alum, and with the iron if present as tanning agent, whereas iron present as a pigment will be in the insolubles together with the clay. The calcium, when present as calcium carbonate, will, of course, be in solution. The magnesium present, as talcum, will be together with the clay and any magnesium salt present, such as Epsom salt, will be in solution.

After filtering off the clay we would go along with the procedure outlined by Dr. Somerville with a fusion method. Of course, some laboratories probably have found other fusion mixtures to be just as efficient as that used in the Rohm & Haas Laboratories. I can recommend as a third ingredient—apart from the sodium potassium carbonate—potassium chlorate, which goes into solution very nicely after cooling.

I want to say one more thing: I believe it is premature to say that colorimetric methods are available in every laboratory for the various metals for which they have been developed, and it is sometimes necessary or desirable to have a volumetric method besides. The titanium, of course, has been always reduced by zinc and zinc alloys and then titrated in the reduced form, which can be done nicely, particularly with perchlorate cerate solution.

It is the intention of the Mineral Leather Committee to work out methods or to expand the methods which are enumerated in our booklet and, as chairman, I would like to ask at this time the members to express their interest in a certain method, and maybe to come to me personally, if they are willing to work on a cooperative study of methods which would enable us to incorporate a zirconium analysis in our Methods Book.

Reactions of Polyamides with Tanning Agents

I. Evidence for the Fixation of Non-ionic Chromium Complexes by the Peptide Groups of Collagen

By K. H. Gustavson and Britta Holm

Introductory

Differentiation of the various protein groups involved in the irreversible fixation of tanning agents by collagen was first attempted in the early twenties by Thomas and his school [1] and by the senior author [2]; investigating the effect of partial inactivation or removal of basic protein groups on the reactivity of collagen.

The primary problem concerns differentiation of the reactions of tanning systems according to the two main types of protein reactions: (1) *Electrovalent* (polar) and (2) *Coordinate* (apolar), using the term coordinate in the original meaning of Pfeiffer [3]. The early findings of Thomas and his coworkers [4], and of the senior author [5] pointed to the participation of non-polar groups of collagen in addition to the polar protein groups in the binding of vegetable tannins. The concept of the function of the non-ionic protein groups, such as the –CO–NH–link, as the coordination center for the polyphenols (tannins) has in recent years received general acceptance (hydrogen bonding). The modern developments have been adequately reviewed in a recent paper [6].

In order to establish which protein groups are specific for any particular tanning agent, collagen with its ionic groups blocked or removed has been studied. The cationic groups of collagen has been partly removed by deamination (ε–aminolysine) ([1; 2; 12]) or by chlorination (guanidyl) ([2; 7].) Complete inactivation of the cationic as well as the anionic groups has been accomplished by irreversible fixation of highmolecular sulfo-acids, specific for the electrovalent groups of collagen and lacking in coordinate reactivity [8]. This modified collagen was used for evaluation of reactions not involving the electrovalent groups of collagen (peptide link).

By pretreatment of collagen with acids, alkalis and various lyotropic agents, it is possible to activate certain protein groups. Their function in various tannages has been studied [9]. A great array of proteins, differing in contents of ionic groups and degree of internal compensations of chains, such as collagen, silk-fibroin, wool-keratin, elastin, muscle-proteins, fibrinogen and several globular proteins have been investigated as to their reactivity to various agents, including tanning agents [10].

Inactivation of Carboxyl Groups

The carboxyl groups have been blocked by cationic chromium complexes for the study of the irreversible fixation of vegetable tannins, quinones and aldehydes [11]. Further, esterification of the anionic protein groups has been tried [12], although the product was highly degraded, due to the repeated severe treatments with dimethylsulfate and methyl bromide. The results are hence of questionable value. However, by means of esterification with methanol according to the procedure of Fraenkel-Conrat and Olcott [13], it is possible to effect practically complete esterification of the free carboxyl groups of collagen in one treatment without objectionably degrading the protein [14].

From comparative data of the reactivity of various chromium compounds towards normal collagen and the esterfied collagen, it is evident that *for the fixation of cationic chromium complexes by collagen ionized carboxyl groups of the protein are required* [14; 15]. The data show further than the non-cationic chromium complexes are fixed by the collagen devoid of carboxyl ions [14]. This was strikingly brought out by series of solutions of 67 per cent acid chromium sulfate containing increasing amounts of sodium sulfite, which addition results in the formation of non-ionic and anionic chromum complexes. At molarities of Na_2SO_3 to Cr_2O_3 exceeding 2 to 1, practically all the chromium exists as non-cationic complexes. Thus, at a concentration of 0.8 eq/1 Cr and 4 hours tanning, hide powder fixed 2.7 meq Cr per g. collagen whereas the methylated hide powder only fixed 0.12 meq. Cr per g. collagen from solutions of 67 per cent acid chromium sulfate, containing 96 per cent of its chromium in the cationic form. From the sulfito-chromium-sulfate, containing 2.5 moles Na_2SO_3 per mole Cr_2O_3, the corresponding figures of chrome fixation

were 4.95, and 6.16 meq. Cr per g. collagen for collagen and esterified collagen respectively [15]. The complex composition of the solution was 86 per cent non-ionic and 14 per cent anionic chromium, positively charged chromium complexes being absent. Hence, the hide powder with inactivated carboxyl groups possesses higher affinity for these non-cationic chromium complexes than the normal hide powder. In the esterification process partial breaking of crosslinks of the protein units (possibly hydrogen bridges between adjacent –CONH–groups) apparently occurs; the final result being a modified protein protein with more easily accessible cationic and non-ionic centers of reaction of the protein. This is evident from the increased fixation of vegetable tannins and irreversibly fixed anions, probably due to the secondary alterations of collagen during the esterification [12; 14].

Polyamides

In view of these findings, it was important to find a substrate containing free –CO–NH–links as the main reactive groups, and devoid of electrovalent groups, or nearly so. Modified Nylons, such as certain Polyamides, meet these requirements as evident from the recent work of Batzer and Weissenberger [16] on the fixation of quebracho extract by a special polyamide. It is important that part of the CONH–groups are not intermolecularly compensated by H-bridging; also that the interstices are large enough to accomodate medium-sized molecules. In fibers of too strongly developed intermolecular linking of the individual chains of the regular type of polyamides-such as Nylon of the original type, the chemical inertness of the polyamide is the result of: (1) the non-availability of coordinate loci on the compensated peptide groups of the tightly and closely aligned molecular chains, and (2) the lack of intermolecular and interfibrillar spaces. The latter means steric hindrance. Earlier investigations of the reaction of tanning agents by means of Nylon, carried out in 1940, showed no or only a slight interaction [17]. More promising was the use of modified silk-fibroin, pretreated in 2 molar solutions of calcium thiocyanate which should cause partial rupture of coordinate crosslinks (H-bonds) [17]. The failure of Nylon and similar polyamides in the form of drawn fibers as a substrate for the study of the function of the peptide groups of collagen in fixation of tanning agents, reported in a recent investigation [18] is thus explicable in view of the parallel alignment of closely packed crosslinked molecular chains with small R–groups (H) in the case of the polyamide, contrasted against the more open structure of the less regular collagen chains with wider intermolecular space and with part of the peptide links not compensated (hydrated). It is also evident that the monotony of the repeating units of the drawn Nylon fiber in its original form –CO–NH $(CH_2)_n$.NH.CO.$(CH_2)_4$.CO–, makes for compactness, insolubility in common organic solvents and chemical inertness; the low moisture content is an example. If side chains are present, the irregularity imparted to the chains

will to some extent ameliorate the chemical inertness. This is also true of copolymers. Further, by the disorganization of the chains and dislocation of a part of the crosslinking H-bonds, induced in dissolving the ployamide in a watermiscible organic solvent (methanol) followed by hydration of the freed non-compensated –CO–NH–groups, a satisfactory degree of accessibility of the structure and a sufficient degree of coordinate reactivity of these groups will be obtained. In the present work, a polyamide of the copolymer type modified in that manner has been employed.

Materials

The polyamide used was *Igamide 6A**, a commercial product of the Badische Aniline & Soda Fabrik, Ludwigshafen a/Rh, Germany, which is a copolymer of the adipic acid-hexamethylene salt (60 per cent), and coprolactam (2 oxo-hexamethylene-imine) (40 per cent)[16]. It is marketed as a colorless, glasslike powder. The original Igamide contained 12.5 per cent N**. and was free from ash (per cent N x 8.0 = per cent polyamide). It contained 97.1 per cent non-volatile matter (100°C.). As evident from the data of Table I, the original polyamide possesses very slight affinity for the coordinate-reacting type of tanning agents. In order to make it more accessible and reactive, it was dissolved in boiling methanol (25 g. polyamide in 750 ml. methanol). The solution was then stirred into cold water in which the polyamide was precipitated in the form of white woolly fibers, very similar to hide powder. The powder was washed thoroughly and mechanically adhering water removed by suction. The shredded preparate was stored and used in this condition. Two batches containing 22.3 and 36.0 per cent dry substance were used.

The hydrated polyamide showed the following characteristics: 12.5 per cent N: 0.0 per cent ash. The HCl-binding capacity at a final pH of 1.05 was 0.5 meq. H^+, and the base binding capacity (NaOH at a final pH of 12.6) 0.02 meq. OH^- per g. polyamide; aqueous suspensions gave a pH of 5.5. The only reactive groups besides the –CO–NH–groups are the cationic and anionic end groups, amounting to 0.07 meq. per g. polyamide. The corresponding value of collagen is 2.0 – 2.1 meq. Hence, the polyamide should be a suitable substrate for investigating reactions involving coordination on peptide groups. The relatively high moisture content of the precipitated polyamide, 12.4 per cent on airdry basis, compared to 2 per cent of the original product, indicates the formation of hydrophilic centers in the structure by the modification. In the dissolution of the polyamide in methanol, part of the H-bonds are probably ruptured and in the following precipitation, hydration of the liberated –CO–NH–groups takes place. Certain similarities to the hydrothermal denaturation of collagen are evident; particularly the

(*) Generously furnished by Professor H. Hopff, Ludwigshafen a/Rh.

(**) The Kjeldahl determination should not be carried out on specimens air-dried at 100°C since by drying at this temperature loss of N will occur (dried *in vacuum* at 40°C.)

disorganization of the chains and the partial rupture of coordinate cross-links (H-bonds)[25].

Results

Table I gives a striking illustration of the importance of the degree of packing of the amide chains and of the amount of available reactive -CO-NH- groups for the behavior of the polyamide towards two chromium compounds, selected on account of their marked affinity for the CO-NH-groups[19]. These aspects of the supermolecular differences are further accentuated by the data from the experiments with two representative vegetable tannins and tannic acid. The average molecular size of these polyphenols is generally considered to be in the range 1000 to 3000[20].

A quantity of hydrated polyamide equal to 0.3 g. dry substance was shaken for 24 hours with 10 ml. portions of the solutions given. Corresponding series were run with hide powder (Lyon) and esterified hide powder for comparison. The preparation and properties of the methylated collagen have been described in another paper[14]. Its *N* content was 17.3 per cent. The treated specimens were washed free from sorbed matter, dried and analyzed for N and Cr. The fixed vegetable tanning material also includes the combined watersoluble matter.

TABLE I

The fixation of tanning agents by polyamides, hide powder and esterified hide powder.

No.	Type of agent	pH value	g/l Cr_2O_3	% non-cationic Cr of total Cr	% Cr_2O_3 fixed on the weight of protein by: Original polyamide	Hydrated polyamide	Hide powder	Esterfied hide powder
1	33% acid Cr-perchlorate phthalate per 1 M	3.4	25.3	71	1.2	7.1	10.5	3.0
2	Phthalato-Cr-sulfate 1 M Cr_2O_3 heated to 60°C, aged 3 months	4.6	20.2	65	0.2	4.5	14.6	7.1
					% fixed tannin, on the weight of protein by			
3	10% solution of Tannic acid	2.8	——	——	0	191	167	208
4	10% solution of Mimosa extract (6.5% w/v tannin)	4.5	——	——	3	114	76	133
5	10% solution of Sulfited Quebracho extract (6.5%w/v tannin)	5.6	——	——	4	87	72	136

The chemical inertness of the polyamide in its original state towards non-ionic chromium complexes and vegetable tannins, both representing the co-ordinative type of reactants is contrasted with the great avidity with which

the same compound reacts with the solute after making the lattice accessible to its molecules and upon activating part of the coordination centers of the potential groups of the polyamide. The solution of the extremely basic chromium perchlorate, mainly composed of non-ionic complexes, which are not so highly aggregated as those of the phthalato-complexed compound [19], shows high binding values of chromium by the hydrated polyamide, compared to the corresponding value of the chromium fixed by collagen. Collagen devoid of free carboxyl groups, which has been shown not to bind cationic chromium complexes [14; 15], will take up non-ionic chromium complexes. This type of fixation is still more prominent for the phthalato-chromium sulfate, whereas the fixation of this compound by the polyamide is relatively low, probably due to obstructed diffusion of rather large phthalato-complexes.

The results from the series of vegetable tannins show that by esterification of collagen the sites of attachment of the polyphenols, probably mainly the –CO–NH–groups, are made more reactive. Rupture of crosslinks of the type of H-bonds and a complete freeing of the basic groups by the inactivation of the carboxyl groups are probably mainly responsible for the maximum reactions of methylated collagen for vegetable tannins, already observed by Bowes and Kenten [12]. The extremely large fixation of vegetable tannins by the hydrated and modified polyamide must be stressed; evidence for the

TABLE II

Fixation of chromium compounds by polyamide and collagen.

No.	Type of compound	g/l Cr_2O_3	pH	% cationic chromium of total Cr	% Cr_2O_3 on weight of protein, fixed by: Polyamide	Collagen
1	100% acid Cr-chloride	15.0	2.5	100	0.0	2.8
2	100% acid Cr-chloride	200	0.6	90	2.0	4.7
3	67% acid Cr-chloride	25.0	2.5	96	1.2	5.7
4	Ditto containing 4 M/1 NaCl	25.0	2.0	90	0.4	8.3
5	25% acid Cr-chloride heated to 100°C; aged 3 months	15.0	3.5	23	0.6	12.2
6	25% acid Cr-chloride *not* heated; freshly used	15.0	3.2	28	2.4	12.8
7	100% acid Cr-perchlorate	15.0	1.8	100	0	2.7
8	67% acid Cr-perchlorate	25.0	2.8	96	0.8	6.4
9	50% acid Cr-perchlorate	25.0	2.9	82	1.3	8.5
10	33% acid Cr-perchlorate	25.0	3.3	29	7.1	12.8
11	80% acid Cr-sulfate	25.0	2.3	96	0.0	4.2
12	67% acid Cr-sulfate $(Cr_2(OH)_2(SO_4)_2.Na_2SO_4$	15.0	3.0	90	0.0	6.3
13	Ditto directly diluted from 250 g/1 Cr_2O_3	15.0	2.6	52	1.0	7.9
14	45% acid Cr-sulfate	15.0	3.1	86	0.3	8.3

prominent role of the –CO–NH–groups for the uptake and binding of tannins (vegetable tannage). These data accentuate the necessity of using hydrated modified polyamides as polypeptide–prototypes in the study of tanning reactions.

The results of the main series are given in Table II. The experimental procedure earlier described was used. Data on the behavior of these chromium salts to esterified collagen are not given, since only the solution which contained large percentages of non-cationic chromium were reactive, i. e., no. 2, 5, 6, 9, 10 and 13. The complex compositions of the solutions were determined by ion exchange, using Dowex–50 in the sodium cycle and Amerlite IRA–400[21].

Discussion

In dilute solutions, the chromium salts of strong acids of acidities >60 per cent consist entirely of positively charged complexes or nearly so[22]. These do not combine with the polyamide, neither with esterified collagen[14], proving the governing role of the carboxyl ions of collagen in the common form of cationic chrome fixation as applied in chrome tanning. In concentrated solutions of these salts, non-ionic chromium complexes are formed[22] and a minor part of these are attached to the polyamide and to collagen which has its carboxyl blocked, as shown by solutions No. 2 and 13. The extremely basic chlorides and perchlorates of chromium contain preponderately non-ionic complexes[22] which readily react with the two last mentioned substrates, indicating, if not proving, other protein groups than the carboxyls to be the loci of binding. The low value of the chromium fixation by the polyamide from the 25 per cent acid chloride (No. 5), aggregated by heating, is probably caused by the obstructed penetration of these large complexes into the lattice. This explanation receives further support by the data of fixed chromium from solution No. 6 which is four times greater than that of No. 5. Solution No. 6 was not heated. It contained smaller complexes than No. 5.

It is rather unexpected to find that by making the solution of the basic chloride (No. 3) 4M in NaCl the chrome fixation by the polyamide is drastically reduced, in view of the fact that the chrome fixation by collagen is markedly increased by this type of neutral salt effect[23]. Inasmuch as neutral chlorides tend to aggregate the basic chromium chlorides[23], the unexpected behavior of the polyamide is very likely due to obstructed diffusion of the enlarged chromium complexes; a steric effect.

Solutions No. 12 and 13 were made up from the same stock solution of $Cr_2(OH)_2(SO_4)_2$. Na_2SO_4, 250 g/1 Cr_2O_3. The only difference is the age of these solutions; No. 12 being aged more than 6 months after dilution, whereas No. 13 was used freshly diluted. In the last instance non-ionic chromium is the main constituent[24] and the polyamide combines with these complexes. On the other hand, the aged solution is inert towards the polyamide, since in the equilibrated solution electropositive chromium is preponderating[24].

The paramount importance of the size of the chromium complexes for their interaction with the polyamide is particularly well brought out by the behavior of sulfito-chromium sulfate to polyamides, collagen and modified collagen. In the introduction, the marked reactivity of non-cationic complexes of sulfito-chromium-sulfate with the esterified collagen was emphasized; the amounts of chromium fixed by the carboxyl-inactivated collagen were greater than those combining with normal collagen. This is also shown by solutions of lower degree of masking, such as those containing 1.5 – 2.0 M SO_3 per M Cr_2O_3, which consist to two thirds of non-ionic and to one third of cationic chromium complexes. Hence, the main reaction apparently occurs between the carboxyl-free collagen and non-ionic complexes. The sulfito-complexes, particularly those containing more than two moles of sulfite per mole chromic oxide, are highly aggregated [5] (gel-forming upon standing) and their reactivity towards collagen is markedly influenced by its previous history, as for instance, the degree of pretreatment with lyotropic agents and by heat denaturation. Thus, the chrome fixation is increased 50–100 per cent by suitable pretreatments as shown in researches of twenty-five years, standing [5]; explained by an additional uptake of the large chromium complexes through coordination on the peptide groups [5]. In view of the highly aggregated state of these complexes, it is not surprising to find that they are only lightly fixed by the polyamide compared to the extremely large fixation effected by the esterified collagen devoid of free carboxyls. The coordinate centers are readily accessible and highly reactive in this instance. In the earlier mentioned case, the polyamide fixed only 0.8 meq. Cr per g. polyamide against 6.16 meq. Cr by the carboxyl-inactivated collagen and 4.95 meq. by normal collagen, per g. protein. Hence, it must be cautioned against drawing too far-reaching conclusions from data from experiments with polyamides, particularly in instances of largely varying molecular size of the tanning agent, since steric effects may materially modify the reactions. Similar complications enter also in the ion exchange technique of examining solutions containing large ions or molecules [19]. It is referred to an earlier finding [10] that the sulfito-chromium sulfate exemplified was only feebly fixed by wool-keratin, 0.5 – 1.0 per cent Cr_2O_3 on the weight of protein. The problem was even then thought to be an example of steric hindrance. The same effect was found for silk-fibroin [10].

Solutions of basic chromum sulfate which have been moderately complexed by means of formiate and oxalate, containing non-ionic complexes as the greatest single constituent, show only slight affinity for the polyamide; values of fixation lower than 1 per cent Cr_2O_3 being recorded. The reason is probably the presence of strong coordinators in these complexes, leaving little coordination power of the chromium atom for the peptide group.

From solutions of basic aluminum sulfate of the type: $Al_2(OH)_2(SO_4)_2 \cdot Na_2SO_4$, at a concentration of 30g/1 Al_2O_3, hide powder fixed 4.8 per cent

Al_2O_3, on the weight of collagen. The corresponding value for the polyamide was 5.4 per cent, and for the esterified collagen 1.6 per cent. Evidently, the greatest part of this fixation is by coordination on non-carboxylic groups, probably on the peptide groups. The participation of such a type of reaction was indicated in the early work on the effect of lyotropic pretreatments of collagen on its tanning potential [9].

Concluding Remarks

The modified polyamide in hydrated state, which practically is devoid of ionic reactivity, offers unique possibilities of assessing the function of its main reactive group, the –CO–NH–link, in protein reactions, since a part of the peptide links are free and moreover easily accessible even to fairly large molecules. However, due regards must be paid to factors such as the molecular size and shape of the solute and the spatial accomodations in the polyamide lattice.

The present survey of the reactivity of basic chromium salts of strong acids towards this peptide prototype shows that their dilute solutions, which mainly contain cationic chromium complexes, are inert towards the polyamide. This lack of affinity is also shown for collagen with its carboxyl groups blocked by esterification. These findings prove the binding of electropositive chromium by hide protein to be effected by its carboxyl ions. The initial reaction is probably ionic, followed by penetration of the carboxyl group into the chromium complex (coordinate-covalent link). Since the polynuclear chromium complexes of the usual type of basic salts, sterically as well as chemically scrutinized, can attach at least two carboxyl groups of adjacent protein chains, on each complex, their function as an exceedingly strong cross-linking agent is secured.

The extremely basic salts and those complexed by means of sulfite, phthalate and other complexing agents contain large amounts of non-ionic chromium. They show a very marked affinity for the polyamide if their molecular size is not too large to retard or block the diffusion of the reactant into the interior of the amide structure and their access to the –CO–NH–groups. Collagen with its carboxyl completely inactivated possesses exceedingly great affinity for those complexes.

Since the only reactive group of any importance in the polyamide is the –CO–NH– group, *the fixation of the non-ionic chromium complexes must be due to non-ionic valency forces, probably coordination on the free –CO–NH–groups.* As mentioned previously this view is corroborated by the earlier findings that this type of chromium compounds shows considerably higher chrome fixation by collagen modified by suitable pretreatments in order to increase its coordinate reactivity (rupture of H-bonds) than by intact collagen (lyotropic salts in concentrated solutions [5]; [10], e. g., calcium thiocyanate, 6 - 8 M urea solution at 35°C [10]; hydrothermal denaturation ([25])). A

similar disorganization of the orderly structure of the molecular chains of the original polyamide, effected by rupturing the intermolecular crosslinks by the solvent (methanol) and the subsequent hydration by the precipitation of the dissolved polyamide, was necessary for securing a reasonable amount of *free* non-compensated –CO–NH–groups of the amide, and spatial accomodation of the tanning agent.

It has also been demonstrated in previous investigations that the coordinate type of chromium fixation by the peptide group ("Molekülverbindungen") does not impart to the collagen lattice the high degree of hydrothermal stability which is associated with the normal reaction of cationic chromium with carboxyl groups in the making of chrome leather[26]. The character of the non-ionic type of coordination tannage is akin to the vegetable tannage, as to stability and physical properties such as feel and stand. The vegetable tannage is generally considered to involve coordinate reactions on the peptide groups[6].

Coordination of non-ionic chromium complexes on the hydroxy groups of collagen (hydroxyproline and serine), present in amounts exceeding the sum of the electrovalent groups, is another possibility.* The effect of the inactivation of the hydroxy groups, by means of sulfation of collagen (in concentrated sulfuric acid[27], and by other means[28], on its chromium fixation is being investigated. The present investigation cannot decide whether the fixation of non-ionic complexes by collagen also involves the hydroxy-groups[29] along with the –CO–NH–groups, the function of which has been proved.

In two following papers the reactions of polyamides in the two-bath chroming process will be treated and further the interaction of polyamide with vegetable tannins and certain syntans. The main reaction of the two bath process is indicated to be an *in statu nascendi* fixation of non-ionic and anionic chromium complexes by collagen ($_{Cf}$[30]).

Summary

Some common types of basic chromium salts, including chlorides, perchlorates and sulfates, of various basicity and complex composition, have been reacted with the hydrated form of a polyamide of the copolymer type containing part of its –CO–NH–groups in the non-compensated hydrated form, easily accessible to the reactants.

Dilute and moderately concentrated solutions of these chromium compounds of acidities >60 per cent, which contain electropositive chromium complexes mainly, do not react with the polyamide, neither with collagen containing its carboxyls blocked by esterification. For this common type of fixation of basic chromium salts by collagen, the presence of carboxyl ions of the protein is an absolute requirement (multipoint coordinate-covalent bridging of adjacent protein chains by their carboxyl groups directly attached to chromium).

*Suggested by Professor John T. Edsall, Boston, Mass., to the senior author in 1948.

From concentrated solutions of these compounds and particularly from solutions of extremely basic chlorides and perchlorates of chromium, preponderantly containing non-ionic complexes, the polyamide as well as the carboxyl-inactivated collagen fix considerable amounts of chromium. Since the ionic function of the polyamide is extremely weak in comparison with its coordinate potency on the non-compensated –CO–NH–groups, this type of chrome fixation must involve the latter groups.

By complexing the basic salts by means of sodium phthalate and sulfite, the cationic chromium complexes are changed into the non-ionic and anionic types. These complexes are fixed by the polyamide, and particularly heavily by the esterified collagen. The size of the complexes enters prominently into the reaction of the polyamide; large molecules, such as the sulfito-complexes, having difficulty of access. It is pointed out that those chromium compounds which are fixed by the polyamide and the modified collagen by coordination on the peptide groups have in earlier investigations been found to be greatly affected in their reactivity with collagen by its previous history, such as lyotropic pretreatment. The changes brought about by the pretreatment have been indicated to be breaking of crosslinks of the H-bond type between protein chains resulting in increased number of coordination active –CO–NH–groups. Hence, by two independent experimental methods evidences are supplied for the participation of –CO–NH–groups of the protein in its binding of non-ionic chromium complexes.

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Resistivity, Dielectric Constant, and Power Factor of Leather

By C. E. Weir

Abstract

Apparent dielectric constants and power factors of leather and hide are reported as a function of temperature and moisture content. Resistivity was measured at 20°C as a function of moisture content. Behavior observed is interpreted as probably arising from interfacial polarization. Data indicate electrical measurments in this frequency range are not reliable for precise quantitative moisture analyses.

1. Introdction

Adsorption of moisture by hygroscopic materials generally causes a marked change in the electrical properties (conductivity, dielectric constant, and power factor) of such substances. This effect is generally attributed to the high dielectric constant and conductivity of the adsorbed moisture as compared to the much lower values exhibited by the dry adsorbate. In view of the large electrical effects produced by the moisture and the rapidity, relative simplicity, and nondestructive nature of electrical measurements, such determinations have been proposed as methods for quantitative moisture determinations [3], [9], [23]. Unfortunately the materials of particular interest in this connection are usually powders or fibrous materials that possess large adsorption surface areas and, therefore, the results of electrical measurements are not easily interpreted because of the complex physical structure of the specimens. Recently, interest has arisen in application of dielectric mesurements for the determination of moisture in leather [21].

This report describes the results of critical studies of the effects of moisture and temperature on the dielectric constant and power factor of leather in the audio and low intermediate frequency range. A complete compilation of the experimental data obtained in these studies is contained in a separate report [38], and only typical data and the essential conclusions are reported here.

In most measurements dealing with a porous material such as leather, two experimental values are recognized, a "real" value associated with the fibers alone, and an "apparent" value which refers to the bulk material including the air in the interstices. This report is concerned only with the apparent dielectric constant and power factor of leather. The real part of the complex dielectric constant as used in this report is not to be associated with the value of the dielectric constant of the leather fibers.

2. Experimental Method

2.1 *Electrical Apparatus*

Measurements of capacitance and resistance were obtained with a precision shielded resistance-capacitance bridge containing a Wagner-earthing circuit. A detailed discussion of this bridge has been published previously [23]. High stability input signals in the frequency range 0.75 KC to 96 KC were provided by a variable frequency oscillator. Bridge balance was ascertained through direct use of earphones at all frequencies as high as 12 KC, while at higher frequencies a regenerative, all-wave receiver was used to detect and amplify the output signals.

Measurements of apparent dielectric constant were made using a shielded, parallel-plate, guard-ring condenser. Electrodes were made of heavy brass plates ½" thick which were given an accurately machined finish. The measuring electrode was 5-7/16 inches in diameter and the normal (empty) plate separation was approximately 0.04 inch. The air capacitance was approxi-

mately 37 $\mu\mu$f. This condenser was used at all frequencies in the range studied and at temperatures varying between 20° C to -70°C. At 0.75 KC balance was obtained to a precision of ± 0.15 $\mu\mu$f and ± 0.0002 ohm, while at 96 KC balance was obtained to within ± 0.01 $\mu\mu$f and ± 0.001 ohm. At frequencies intermediate between these values the precision of balance appeared to vary linearly.

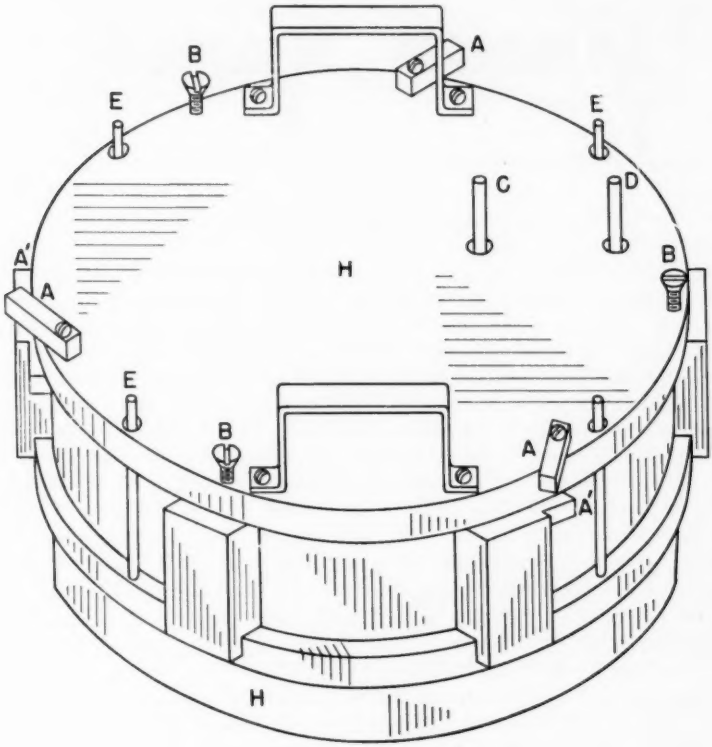

FIGURE 1.—The condenser: A–external view.
A, A'–projecting ears used for measurement of spacing.
B –set screws for adjusting spacing.
C –connection to guarded electrode.
D –connection to guard ring.
E –guide rods for movable electrode mounting.
F –connection to high potential electrode.
G –bakelite insulation.
H –grounded brass shield.

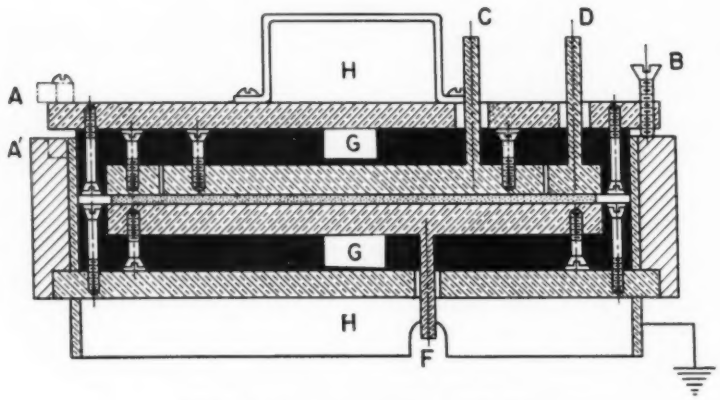

FIGURE 1.—The condenser; B–cross section.

The shield of the condenser was equipped with two sets of three projecting ears spaced at angles of 120° on its periphery, one set on the top or movable plate, the other directly below on the frame of the condenser. These ears were used to measure the plate spacing, measurements being made to the nearest 0.0001 inch by means of micrometers. Such measurements were made at the conclusion of electrical studies on each specimen. Three set screws mounted in the top plate, equidistant between the ears, permitted resetting the empty condenser to the same spacing measured when the test specimen was in the condenser. The spacings were reproduced to within ±0.0002 inch at each ear and the average of the three settings was reproduced to ±0.0001 inch. Measurements on the empty condenser under these conditions were used to determine the air capacitance—assumed equal to the vacuum capacitance. In all measurements the top plate of the condenser which weighed 15 pounds was loaded with an additional 20 pounds to improve the contact between specimen and plates. The external construction and a cross section of the condenser are shown in Figs 1A and 1B respectively.

The real part of the dielectric constant, designated as ϵ', was obtained as the ratio of the capacitance of the condenser containing the specimen to that of the empty condenser with the same plate separation. The power factor, designated as cos ϕ, was obtained from the relationship

$$\cos \phi = 1 / \sqrt{1 + (R_p \omega C_p)^2}$$

where R_p is the equivalent parallel resistance of the condenser containing the specimen, C_p its capacitance, and ω the angular frequency. The empty condenser exhibited no losses in this frequency range, therefore, all losses observed were associated with the test specimens.

2.2 *Test Specimens and Conditioning*

Disks 6¼ inches in diameter of chrome hydraulic packing leather, vegetable crust leather, and unhaired cowhide were split to a uniform thickness of approximately 4 mm ± .02 mm by removing portions of grain and flesh layers on a band knife splitting machine. The disks were degreased, washed, and dried exhaustively in vacuo. All tests were performed on a single specimen of each type of leather.

Initial measurements were made on dry specimens which were then permitted to adsorb moisture from the air to obtain moisture contents as high as approximately 15 per cent. For higher moisture contents specimens were exposed to vapors existing above suitable saturated salt solutions or water. Moisture contents below approximately 10 per cent were obtained by short (a few minutes to as much as 1 hour) exposures to conditioned air. Uniform moisture distribution was unlikely under these circumstances but no appreciable change in capacitance or resistance which might be attributed to redistribution of absorbed moisture was noted during measurements which required as long a period as 48 hours. Above 10 per cent moisture, exposures to conditioned atmospheres were conducted for at least 18 hours. Despite the longer exposures appreciable variations in both capacitance and resistance were noted in periods of less than 1 hour. Moisture contents were obtained by weighing specimens in a sealed container made of polyethylene film and are based on the dry weight of the specimen. At low moisture contents specimens gained and at high moisture contents lost moisture during introduction and removal from the condenser. Therefore, weights were obtained before and after study, and the average of the two weights was taken to represent the moisture content during measurement. In most instances the change in weight noted corresponded to less than 0.1 per cent moisture.

2.3 *Effect of Temperature*

All measurements below room temperature were made in a double-walled insulated container. The parallel-plate condenser and its external loading weight were placed in the innermost container which was then covered. An ice-water bath, or a dry ice-acetone bath was placed in the outer container to obtain the desired low temperature. Temperatures were measured with a copper-constantan thermocouple mounted inside the condenser. The reference junction of this thermocouple was maintained at 0°C. Measurements on specimens were generally made after exposure to the desired temperature for 6 hours, and although thermal equilibrium was usually not attained in this time, the change in temperature during the time required for measurements was negligible.

3. Results

3.1 *Apparent Dielectric Constant and Power Factor*

(a) Effect of Moisture

Typical measurements on untanned leather of various moisture contents are given in Table 1. The results obtained on chrome and vegetable leathers are analogous in all respects to that of the hide.

TABLE 1

Untanned Hide
Apparent dielectric constant and power factor
Temperature 22.25°C.

Frequency	Dry		2.83% H_2O		5.64% H_2O		8.52% H_2O		11.3% H_2O	
KC	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ
0.75	1.91	0.0132	2.04	0.0119	2.23	0.0182	2.47	0.0205	2.79	0.0256
1.5	1.90	0.0135	2.03	0.0153	2.22	0.0180	2.46	0.0224	2.76	0.0251
3.0	1.88	0.0129	2.02	0.0159	2.21	0.0180	2.44	0.0202	2.73	0.0241
6.0	1.87	0.0132	2.00	0.0161	2.19	0.0182	2.42	0.0206	2.71	0.0238
12.0	1.86	0.0124	1.99	0.0164	2.18	0.0190	2.40	0.0212	2.68	0.0249
24.0	1.85	0.0117	1.97	0.0168	2.15	0.0196	2.37	0.0219	2.65	0.0253
48.0	1.84	0.0112	1.96	0.0173	2.13	0.0208	2.35	0.0234	2.60	0.0267
96.0	1.83	0.0101	1.94	0.0163	2.12	0.0206	2.33	0.0232	2.58	0.0248

Frequency,	14.9% H_2O		19.7% H_2O		31.7% H_2O		40.3% H_2O	
KC	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ
0.75	3.27	0.0261	4.33	0.0757	10.58	0.578	19.80	0.897
1.5	3.24	0.0245	4.24	0.0572	10.29	0.428	16.52	0.810
3.0	3.22	0.0234	4.17	0.0445	7.80	0.388	13.81	0.707
6.0	3.18	0.0236	4.12	0.0380	6.94	0.309	11.60	0.593
12.0	3.16	———	4.06	0.0335	6.35	0.235	10.02	0.478
24.0	3.12	0.0247	4.01	0.0322	5.95	0.171	8.86	0.367
48.0	3.09	0.0265	3.95	0.0328	5.69	0.126	8.04	0.274
96.0	3.05	0.0265	3.90	0.0316	5.51	0.0911	7.50	0.192

The following typical behavior is noted in the data of Table I:

ϵ' increases with increasing moisture content at all frequencies.

ϵ' decreases with increasing frequency at all moisture contents, the frequency dependence being least for dry material and greatest for moisture contents of 15 per cent or more.

Cos ϕ increases with increased moisture content.

Cos ϕ appears to be relatively frequency independent until high moisture levels are reached, i. e. 15 per cent or more. The small changes in cos ϕ with change in frequency noted at low moisture contents are, however, too large to be attributed to experimental errors.

Cos ϕ decreases strongly with increasing frequency at higher moisture levels.

For moisture contents below approximately 15 per cent, all measured capacitances and resistances appeared to be independent of time, being re-

producible to within 0.1 per cent after several hours. At moisture contents greater than 15 per cent, definite time dependence was noted, the effect being an increased capacitance and in most instances a decreased power factor at a constant frequency with increasing time. Such effects caused no appreciable error in the measured values, since the changes occurring during the hour required for measurement were generally much less than 1 per cent.

(b) *Direct current resistance*

To ascertain the volume resistivity of the test specimens and the magnitude of corrections to the effective AC resistance of the condenser containing the specimen, direct current resistance measurements were carried out on chrome and vegetable leathers immediately following the dielectric measurements.

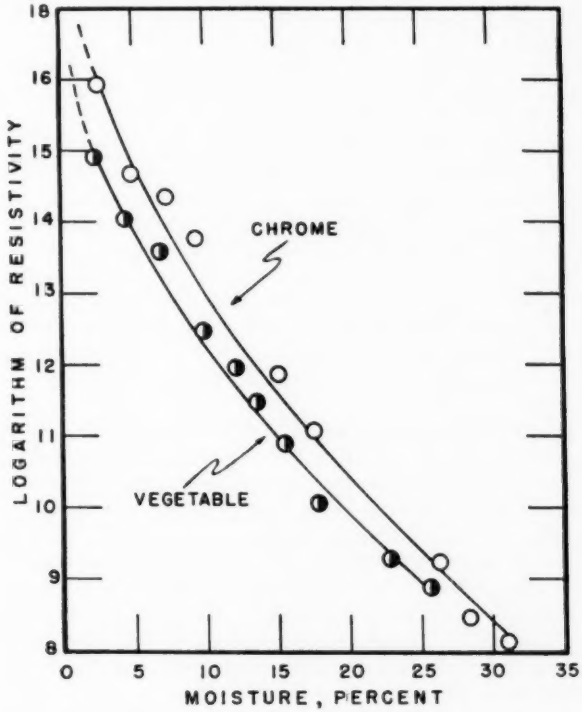

FIGURE 2.—Effect of moisture content on volume resistivity of chrome and vegetable leathers.

A commercially available megohm bridge containing a guard circuit was used in these studies, all measurements being conducted at room temperature (20–25°C) with an applied voltage of 500 VDC. The results of these measurements calculated in terms of resistivities are shown graphically in Fig. 2.

It will be noted that the resistivities are rather high even at higher moisture contents. The magnitude of these values is such that at room temperature no significant correction for D. C. resistivity is required, since A. C. resistivities were invariably many fold larger than the DC values. It was also observed that the resistance was independent of time at low moisture contents, but at higher moisture levels a time dependent drift of resistance to higher values was noted.

(c) *Effect of temperature and moisture*

To obtain further information on the phenomena responsible for the observed behavior of ϵ' and cos ϕ at room temperature, as well as data on the temperature dependence of these quantities, measurements were made at room temperature and at approximately 0°C and -70°C. As noted previously, thermal equilibrium was generally not attained at reduced temperatures so that measurements were conducted with a very slowly decreasing temperature, the actual temperature being measured thermoelectrically. Prior to each measurement at a reduced temperature, a set of data was obtained at room temperature, in order to ascertain any hysteresis effect resulting from a previous cooling. In general, measurements were conducted at 0°C before cooling to -70°C, but in some instances this order was reversed since the experiments indicated hysteresis effects did not affect the general nature of the experimental results. Typical results of these experiments for untanned hide are given in Table 2, the sets of data obtained at room temperature being given in the columns to the left of the succeeding data obtained at reduced temperatures.

Apparent dielectric constants shown in this table were obtained by use of the air capacitance of the condenser as measured at room temperature, since it was not feasible to measure the plate separation while the condenser was subjected to low temperatures. A measure of the error involved in this procedure may be obtained by manipulations of the equation for the capacitance of a parallel plate condenser and use of the coefficients of thermal expansion of brass[12] and leather[37]. For the experimental quantities involved here such calculations indicate an error of 1.4 per cent in ϵ' and cos ϕ for a temperature change of 100°C. Since comparative data are of major interest here, such an error will in no way affect the conclusions to be drawn from these data, which are as follows:

ϵ' decreases with decreasing temperature at all frequencies and moisture contents, and is strongly temperature dependent at high moisture levels.

ϵ' decreases with increasing frequency at all temperatures and moisture contents.

Cos ϕ generally decreases with decreasing temperature at a fixed frequency for very low and very high moisture contents, being strongly temperature dependent at higher moisture levels.

At intermediate moisture contents cos ϕ may increase or decrease with decreasing temperature depending on frequency and temperature.

TABLE 2

Effect of Temperature and Moisture on Apparent Dielectric Constant and Power Factor of Hide Collagen

	Dry Hide							
Frequency KC	20.5° C		−70.0° C		22.0° C		2° C	
	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ
0.75	1.88	0.00976	1.74	0.00198	1.88	0.00912	1.84	0.0155
1.5	1.88	0.0155	1.71	0.00365	1.88	0.0137	1.84	0.0113
3.0	1.87	0.0153	1.71	0.00400	1.87	0.0148	1.83	0.0139
6.0	1.86	0.0147	1.70	0.00473	1.86	0.0145	1.82	0.0130
12.0	1.84	0.0140	1.70	0.00474	1.85	0.0140	1.81	0.0123
24.0	1.83	0.0133	1.70	0.00441	1.84	0.0133	1.80	0.0112
48.0	1.82	0.0130	1.69	0.00429	1.83	0.0127	1.79	0.0105
96.0	1.81	0.0113	1.69	0.00377	1.82	0.0113	1.78	0.0093
	16.0% H_2O							
	22.5° C		−68° C		23.0° C		2° C	
	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ
0.75	3.27	0.0286	2.42	0.0281	3.22	0.0291	3.03	0.0208
1.5	3.24	0.0263	2.40	0.0259	3.19	0.0286	3.01	0.0243
3.0	3.21	0.0249	2.37	0.0291	3.15	0.0263	2.99	0.0237
6.0	3.18	0.0251	2.33	0.0303	3.12	0.0256	2.95	0.0241
12.0	3.14	0.0252	2.30	0.0319	3.08	0.0249	2.93	0.0255
24.0	3.10	0.0263	2.26	0.0323	3.05	0.0263	2.89	0.0263
48.0	3.07	0.0279	2.22	0.0313	3.01	0.0279	2.86	0.0283
96.0	3.03	0.0277	2.18	0.0326	2.97	0.0279	2.83	0.0282
	37.1 % H_2O							
	22.4° C		−74.7° C		22.1° C		0° C	
	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ	ϵ'	cos ϕ
0.75	19.20	0.773	4.07	0.0720	19.60	0.825	11.70	0.610
1.5	14.96	0.701	3.97	0.0735	15.11	0.747	9.79	0.502
3.0	12.00	0.614	3.83	0.0854	12.22	0.650	8.58	0.385
6.0	9.90	0.520	3.69	0.0953	10.20	0.535	7.79	0.283
12.0	8.54	0.412	3.52	0.1078	8.90	0.413	7.29	0.200
24.0	7.66	0.305	3.34	0.1178	8.06	0.300	6.95	0.141
48.0	7.08	0.221	3.15	0.1275	7.50	0.215	6.69	0.106
96.0	6.74	0.153	2.98	0.0617	7.15	0.148	6.51	0.0805

At low temperature and high moisture contents cos ϕ (as well as ϵ'') exhibits a somewhat broadened but unmistakeable absorption maximum, for hide and vegetable leathers while such a maximum would appear to be present in chrome leather at higher moisture contents than those studied.

4. Discussion

4.1 *Electrical Properties of Collagen and Leather*

Resistivity data reported here are similar to results previously reported on cellulose products which have been extensively studied in view of their widespread electrical applications. However, results obtained here for leather exhibit no linear relationship between logarithm of resistance and any simple function of moisture content as has been reported for textiles and cotton [27, 29, 36]. This divergence may be associated with the greater adsorptive capacity of leather for moisture or with differences in the mechanisms of adsorption in these materials.

Apparent or bulk dielectric constants of moist leather have been reported by Compton [5] who used a bridge method at 1 kc. His experimental values are much larger than those reported here at comparable moisture contents. This fact together with his extremely high values of dielectric constant - ϵ' as high as 4980 - have been considered in reaching conclusions drawn from these data. Neither Compton nor Kremen [20, 21] investigated the effects of temperature of frequency on ϵ' and neither studied power losses, although Compton concluded that resistance measurements made during his measurements showed such little concordance that their use did not seem justified.

The data obtained here are similar in many respects to previous reports of effects of adsorbed vapors on the electrical properties of other porous materials [1, 6, 17, 18, 19, 24, 28, 35]. In view of the similarities in results and the characteristics of the materials, the interpretations of the present data are patterned to some extent along the lines of the conclusions of previous workers [6, 8, 17, 27, 28, 31, 34] who have emphasized the imporatnce of considering interfacial polarization in electrical measurements on non-homogeneous materials of this type.

Leather must possess a large adsorption surface area by virtue of its fibrous structure. This area has been calculated by Kanagy [15] from adsorption data. Since the fibers are composed of submicroscopic fibrils and moisture appears to penetrate the fibers, it would appear that the fibrillar surface area must play a role in these data. The filaments which make up the fibrils may also be involved, but qualitatively the conclusions reached here will be independent of the units involved. There are probably three phases present in moist leather—the leather substrate which may contain combined or dissolved moisture, a surface layer of adsorbed moisture, and the surrounding air. The interface between any two of these phases is an obvious source of Maxwell-Wagner polarization effects. The behavior of such types of interfacial polari-

zation has been considered in detail and developed quantitatively for simple systems by other workers[25, 30, 31]. In leather the vast number of these interfaces present, the complexity of the interconnections of the physical matrix, and the unknown conductivities and dielectric constants of the phases involved present a problem that permits no quantitative analysis. The only facts available are that the dielectric constants of the three phases are quite different in bulk form, while the conductivity of the air will be much less than that of either the moist substrate or the adsorbed moisture layer. Wagner[31] has shown that a necessary condition for minimizing interfacial effects is that

$$\sigma' \epsilon', = \sigma_2 \epsilon'_2$$

where σ and ϵ' are conductivity and dielectric constant respectively, and the subscipts refer to the phases which form the interface. In the present situation it is extremely improbable that such a relationship will hold at the three possible interfaces at all moisture contents studied.

A somewhat different type of polarization known as electrode polarization may exist at the discontinuity between specimens and the condenser plates. In the present experiments no differentiation between electrode polarization and the interfacial polarization existing within the specimen is possible, and the electrode polarization will be considered as lumped with the interfacial effects.

The other important type of polarization arises as a result of the numerous permanent dipoles known to be present in the basic protein by virtue of its amino acid composition. These dipoles will represent sources of Debye polarization, an effect that is qualitatively similar to interfacial polarization. The extreme difficulty in distinguishing between these two phenomena has been emphasized previously[25, 30].

As a result of the experimental data obtained in these studies the following general picture may be given. In the dry condition in this frequency range, leather may be considered to have a dielectric behavior which is characterized by a moderate power absorption with slight frequency dependence. As the moisture content of the leather increases, two dielectric absorption maxima—one at very high, the other at very low frequencies outside the frequency range used here—appear and increase in magnitude with increasing moisture content. The high frequency maximum grows the more rapidly at low moisture contents, and at very low moisture contents largely determines the behavior of the leather. As moisture is added the low frequency, or interfacial effect, grows at an increasing rate, and in the moisture range 5–15 per cent losses due to both types of dielectric absorption are determining factors. In this moisture range at room temperature the data may be pictured as being taken in the trough between the two dielectric absorption maxima. As the moisture content rises above about 15 per cent, the rate of growth of the interfacial region accelerates tremendously, and at high moisture contents the

enormous size of the power absorption arising from interfacial effects completely overshadows the smaller but probably still important maximum at higher frequencies. The source of the low frequency losses has been attributed to interfacial charging phenomena, and it remains to consider the causes of the losses at higher frequencies. The high frequency absorption may be due to dipolar polarization or to a different type of interfacial phenomenon. Since dipoles are known to be present in the protein, it would seem that the power absorption may be due to such causes. The increasing importance of this absorption with increasing moisture content, noted at low moisture contents but probably occurring even at high moisture contents, may be considered as due to increased mobility of the existing dipoles conferred by the imbibed moisture. The dipoles in the dry material may be thought of as being largely immobilized by the compact molecular structure of dry collagen with correspondingly large restraining forces. Since the compact structure relaxes in the presence of moisture, these bound dipoles may be freed to some extent, the degree of freedom increasing with increasing moisture content.

The absorption maximum observed at low temperatures and high moisture contents may not be positively identified with any specific mechanism. This maximum may arise from the dipolar polarization which has been shifted to lower frequencies as a result of the decrease in temperature or it may be due to ice which is known to exhibit an absorption maximum in this range [7, 26, 32].

The interpretation of these data given in the foregoing implies a somewhat different role of moisture in the low and in the high moisture ranges, with a gradual shift of the effect centering at approximately 15 per cent moisture. This behavior is clearly shown by ϵ' and cos ϕ in the tabular data. The gradual transition region is observed to occur at lower moisture contents in vegetable leather than in chrome leather or in hide, and may be directly related to that moisture content range in which the slope of the heat of adsorption curve is undergoing its greatest change [13]. The apparent difference in effects of moisture in the low and high moisture range may be considered to be due to the decreased binding energy of the moisture with increasing moisture content. Such concepts have been advanced previously [1, 28].

This difference in behavior of moisture in the two moisture ranges may be related to concepts of "bound water" which have been discussed by numerous workers [2, 10, 11, 13, 14], and with particular reference to leather by Compton [5], Kremen [22], and Cheshire and Holmes [4]. These latter workers conclude that between 30 and 50 per cent of moisture on a hide substance basis can be considered as "bound water". The present studies were conducted principally in the range of moisture contents in which these workers would consider all moisture present to be bound.

The present data show that the moisture present in small amounts produces a markedly different effect than that present in large quantities. Below a

rather ill defined transition region centering at about 15 per cent moisture, the principal effect is the enhancement of the high frequency dielectric adsorption, while interfacial polarization is effected to a rather small degree. In this range the moisture might be considered to be mainly intimately associated with the protein, probably by means of chemical forces through hydrogen bonding. Relatively little moisture is therefore available to act electrically as one might expect water to behave.

At the higher moisture contents the effect of moisture on the high frequency dielectric absorption is masked by the rapid growth of the interfacial polarization. In this range the principal effect appears to be on the surface of the structural units involved so that conducting layers are rapidly built up to produce the interfacial effects observed. In this range the moisture produced electrical results which might be expected of water.

It is possible therefore to distinguish between these two essentially different roles of moisture, even in the range in which all moisture has been considered to be bound. It must be concluded that there is considerable difference in binding of the so-called bound water.

The detailed qualitative analysis of the data which produced the previous conclusions as well as the complete experimental data are contained in a separate publication [38].

5. Determination of Moisture in Leather by Electrical Methods

From the data obtained in these studies it follows that in this frequency range electrical methods can not be expected to yield precise results in quantitative analyses for moisture. To test this conclusion an experiment was per-

TABLE 3

Reproducibility of Electrical Data on Specimens from Different Hides of the Same Tannage*

Specimen	Commercial Leather				Degreased Leather			
	Thick. in.	Condenser Plate separation in. (measured from arbitrary zero)	ϵ'	cos ϕ	Thick. in.	Condenser Plate separation in. (measured from arbitrary zero)	ϵ'	cos ϕ
1	0.093	1.1057	3.29	0.0275	0.094	1.1079	3.26	0.0521
2	0.094	1.1040	3.35	0.0356	0.094	1.1071	3.18	0.0485
3	0.094	1.1059	3.43	0.0382	0.094	1.1075	3.41	0.0805
4	0.090	1.1078	3.18	0.0269	0.092	1.1037	3.10	0.0448
5	0.094	1.1060	3.42	0.0444	0.095	1.1087	3.38	0.0599

Standard deviation for ϵ' commercial — 0.10
Standard deviation for ϵ' degreased — 0.13
* measurements at 3KC.

formed on similar specimens of commercial, fat-liquored, chrome upper leather which were cut from corresponding areas of different hides of the same tannage. All specimens were cut from similar positions in the shoulder region, and were selected for uniformity of thickness over the area of the test piece. Following initial measurements, the specimens were degreased and rerun to ascertain the effects of inequalities in grease content. The results of these measurements are given in Table 3.

Thickness measurements are the average of 15 determinations distributed uniformly over the area of the test specimen. These measurements were made to the nearest 0.001 inch. Condenser plate separations are the average of three measurements made as described previously, and are accurate to the nearest 0.0001 inch. Differences noted in ϵ' and cos ϕ are real, since the experimental capacitances and resistances involved were measured to at least four significant figures.

Variations noted in ϵ' and cos ϕ indicate that use of these quantities to characterize or measure the moisture content would be subject to considerable uncertainty in an arbitrary piece of leather. Measurements of moisture contents of these specimens have not been made, since all specimens were subjected to identical treatments throughout, and experience in this laboratory has shown that a moisture content of about 15 per cent with a variation of less than approximately 1 per cent may be expected for such specimens from the same location of different hides of the same tannage. Since some differences of apparent density or fiber orientation exist, the variations observed in ϵ' and cos ϕ are not considered excessive.

It is concluded therefore that in this frequency range electrical methods are not expected to produce precise quantitative determinations of moisture in leather. Although this conclusion is reached largely as a result of data accumulated using alternating currents, it is believed that the same considerations apply to direct current measurements. This extension of the conclusions appears to be valid as a result of observations made previously concerning behavior of the direct current resistance of specimens containing moderate amounts of moisture. For rapid, nondestructive estimates of moisture content, particularly for control work, such methods may be adequate, provided the effects of temperature and salt content are recognized and controlled..

6. Summary

Apparent or bulk dielectric constants and power factors of chrome and vegetable leather and untanned hide were studied for moisture contents up to approximately 40 per cent, at temperatures of 23°C, 0°C, and –70°C over the frequency range 0.75–96KC. Apparent dielectric constant decreases with frequency and temperature at all moisture contents, the frequency dependence increasing with increasing moisture content. Apparent power factors generally exhibit similar behavior. At –70°C at high moisture contents, a

diffuse absorption observed may be due to ice or to permanent dipoles of collagen which are freed by moisture. Observed behavior is interpreted as probably arising from a combination of interfacial polarization at surfaces existing in the fibrous leather and dipolar polarization. Apparent D. C. volume resistivity decreases from values $>10^{16}$ ohm-cm when dry to values $\simeq 10^{9}$ ohm-cm at 30 per cent moisture. Results indicate electrical measurements in this frequency range are probably not reliable for precise quantitative moisture analyses.

7. Acknowledgment

The author is indebted to C. G. Malmberg and A. A. Maryott for use of the capacitance bridge which made these measurements possible, as well as for the stimulating discussions directed toward understanding of this problem.

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Variations of Physical and Chemical Properties Within and Between Vegetable Retanned Cow and Steer Sides**

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Abstract

A previous study on the sampling of military upper leather was made on split and unsplit side leather . In the present paper this study is extended to chrome-retanned side leather. Since the customary procedure for making military upper leather involves the retanning process, these results were considered highly important as a basis for accepting a final sampling procedure. Cow and steer sides were used to determine if any important differences in the physical properties of the hide could be attributed to the sex of the animal.

The only significant difference in physical properties between the cow and steer sides is a higher tensile strength shown by the former. Chrome-retanned leathers are more uniform in thickness and have a less variable grease content than chrome-tanned leathers. They are, however, weaker in strength and less water resistant than chrome-tanned leathers. The higher water vapor permeability of the retanned leathers probably enhances their comfort to the wearer to a small extent.

1. Introduction

A previous study on the sampling of military upper leather was made on split and unsplit chrome tanned side leather[1]. In the present paper this study is extended to chrome retanned side leather. The chrome retanned leathers were prepared from sides from cows and steers. Since the customary procedure for making military upper leather involves the retanning process, these results were considered highly important as a basis for accepting a a final sampling procedure. A study of the properties of this type of leather would also have greater practical significance. Studies were made with cow

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and steer sides to determine if any important differences in the physical properties of the hide could be attributed to the sex of the animal.

2. Sampling Areas and Selection of the Test Specimens

The method of determining the cutting or sampling area of the sides is the same as that described in the report on the split and unsplit chrome tanned sides [1]. The original areas of the sides and the dimensions of the cutting areas are given in Table I. The steer sides are on the average longer than the cow sides.

The sides were sampled for tests by the same procedure as described in [1]. This plan for cutting the blocks and the specimens for test is reproduced in Figure 1 for the convenience of the reader of this paper.

TABLE 1

Areas of Original Hides and Dimensions of Test Areas of Cow and Steer Hides

Hide		Original Areas		Cows			Steers		
Cows	Steers	Cows	Steers	AB	BD	AC	AB	BD	AC
		ft²—¼ ft²	ft²—¼ ft²	in.	in.	in.	in.	in.	in.
A	Q	22+3	25+0	73.0	30.0	21.0	75.0	34.0	22.0
B	R	19+2	22+1	70.6	28.0	20.5	71.5	31.0	21.5
C	S	20+1	22+1	70.0	30.0	21.0	73.0	31.0	22.0
D	T	21+2	19+3	71.3	30.0	22.5	68.0	30.0	21.0
E	U	18+1	25+2	71.0	30.0	21.6	76.0	32.0	25.0
F	V	20+2	20+3	70.0	30.0	20.0	78.0	34.0	21.0
G	W	22+1	26+0	71.0	30.8	22.2	70.0	30.5	20.0
H	X	19+0	24+2	67.0	29.8	20.0	74.8	30.0	22.0
J	Y	23+2	23+2	70.0	33.0	22.4	74.0	31.0	21.0
K	Z	23+3	25+0	73.0	30.4	22.2	79.0	31.0	20.5
L	XA	21+3	23+2	72.0	34.0	22.0	73.0	32.0	22.0
M	XB	20+3	24+2	70.0	30.5	20.2	73.0	30.0	22.0
N	XC	23+1	25+2	74.0	31.0	21.5	73.0	31.0	24.0
O	XD	22+0	20+2	72.0	31.0	22.0	70.0	30.0	21.0
P	XE	21+3	22+1	71.0	30.8	22.0	71.0	30.8	20.5
Average		21+3	23+3	71.1	30.6	21.4	73.3	31.2	21.7

Fifteen cow sides and fifteen steer sides were used in these tests. The tests applied were the same as those used in the study of the split and unsplit chrome tanned sides [2]. Several modifications on the number of specimens used in the tests were, however, made on the basis of information gained from the latter study. Only seven tests for water vapor permeability and for water resistance on each side were made. This permitted the performance of more burst tests per hide. The tests on the split and unsplit leathers indicated

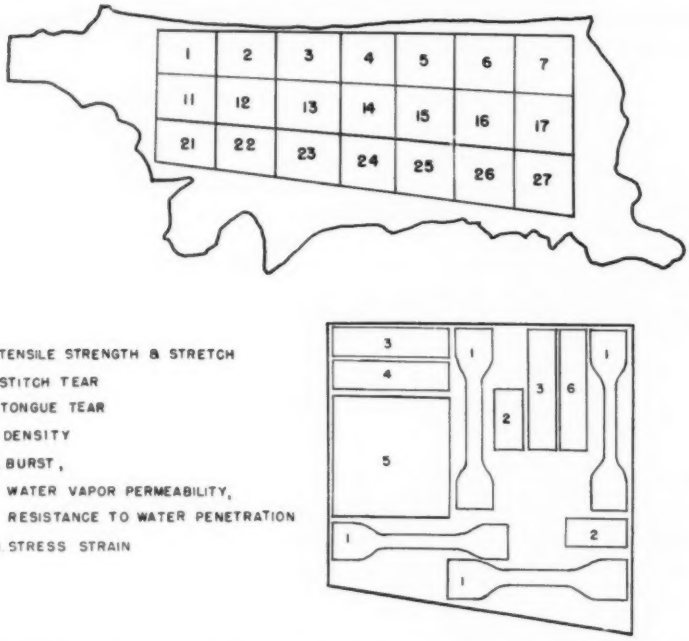


FIGURE 1.—Design used in cutting test specimens from blocks cut from the sides.

that the chemical analysis could be made sufficiently precise by the sampling of four hides. Chemical analysis was therefore made only on four of the steer sides and four of the cow sides. Physical tests used were tensile strength and elongation, stitch tear, tongue tear, and burst. Samples for chemical tests were taken from the unused portions of the blocks and from the broken tensile strength specimens.

3. Test Methods

The test methods used are described in Federal Specification KK-L-311, with a few exceptions. Water penetration was measured by the dynamic method developed by Maeser [3]. The strength tests—tensile, stitch tear, tongue tear, and burst—were made on a Tinius Olsen testing machine [4], which by proper adjustment of the loading range afforded a high degree of accuracy at any required load. A special adapter was developed for use with this machine for measuring bursting strength, which is described in [1]. Water vapor permeability was measured by the method developed by Kanagy and Vickers [5].

4. Results and Discussion

The results are presented in the form of hide and block averages in the ensuing tables and figures. Lack of space for publication did not permit the presentation of each individual test determination.

TABLE 2

Side Averages for Cow and Steer Sides

Hides		Tensile Strength				Stitch Tearing Strength			
		⊥		∥		⊥		∥	
Cow	Steer	Cows	Steers	Cows	Steers	Cows	Steers	Cows	Steers
		lb/in²	lb./in²	lb/in²	lb/in²	lb/in thick	lb/in thick	lb/in. thick	lb/in. thick
A	Q	327x10	313x10	400x10	344x10	103x10	89x10	133x10	95x10
B	R	401	292	475	368	102	96	100	107
C	S	361	294	427	367	95	92	103	104
D	T	315	320	356	333	93	103	95	101
E	U	367	278	461	325	91	76	94	93
F	V	326	318	378	346	87	98	103	107
G	W	297	337	362	416	84	93	96	105
H	X	356	304	410	368	102	89	110	102
J	Y	293	369	364	409	83	104	94	113
K	Z	331	278	387	330	94	87	101	98
L	XA	388	257	449	286	102	82	110	100
M	XB	335	285	377	317	95	98	103	107
N	XC	335	309	387	383	94	97	95	109
O	XD	353	335	408	348	91	99	97	103
P	XE	335	259	395	297	97	88	99	103
Average		341	303	402	349	94	93	102	103

Hides		Tongue Tearing Strength				Bursting Strength		Grain	Crack
		⊥		∥					
Cows	Steers	Cows	Steers	Cows	Steers	Cows	Steers	Cows	Steers
		lb/in thick	lb/in thick	lb/in. thick	lb/in thick	lb/in thick	lb/in thick	lb	lb
A	Q	41x10	40x10	38x10	40x10	1030x10	1002x10	424	439
B	R	42	44	40	39	1150	980	509	422
C	S	43	41	40	38	1061	989	528	414
D	T	36	46	35	39	844	1063	360	476
E	U	38	35	38	34	1051	853	696	334
F	V	43	48	37	41	959	1004	484	534
G	W	34	42	35	38	864	1086	379	676
H	X	44	42	42	41	1043	966	494	552
J	Y	41	46	34	43	839	1058	438	584
K	Z	43	39	36	36	939	855	360	399
L	XA	46	36	42	33	1113	897	599	376
M	XB	40	41	38	44	1011	1032	412	470
N	XC	36	51	35	41	962	1054	398	452
O	XD	39	48	37	46	945	1054	461	589
P	XE	36	41	42	43	1004	995	422	453
Average		40	43	37	40	988	993	464	478

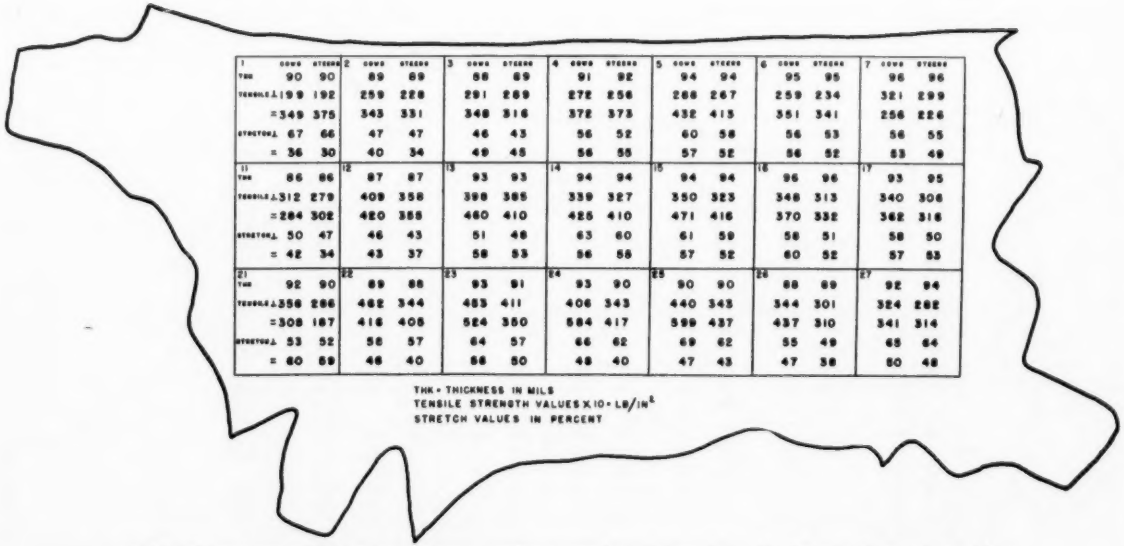
TABLE 2 (Continued)

Hides		Elongation at Break ⊥		Elongation at Break ∥		Thicknesses	
Cow	Steer	Cows	Steers	Cows	Steers	Cows	Steers
		%	%	%	%	mils	mils
A	Q	57	50	51	47	95	96
B	R	56	60	52	46	91	90
C	S	58	53	50	44	91	93
D	T	52	50	48	44	92	89
E	U	60	53	52	45	95	91
F	V	55	60	51	52	92	96
G	W	65	54	52	47	94	89
H	X	57	57	50	50	87	94
J	Y	56	55	54	49	95	88
K	Z	62	53	55	45	89	89
L	XA	56	53	49	42	93	91
M	XB	59	50	51	45	89	90
N	XC	55	56	46	48	90	95
O	XD	54	55	50	47	90	91
P	XE	60	52	55	44	92	90
		—	—	—	—	—	—
Average		57	54	51	46	92	91

4.1 *Physical Properties*

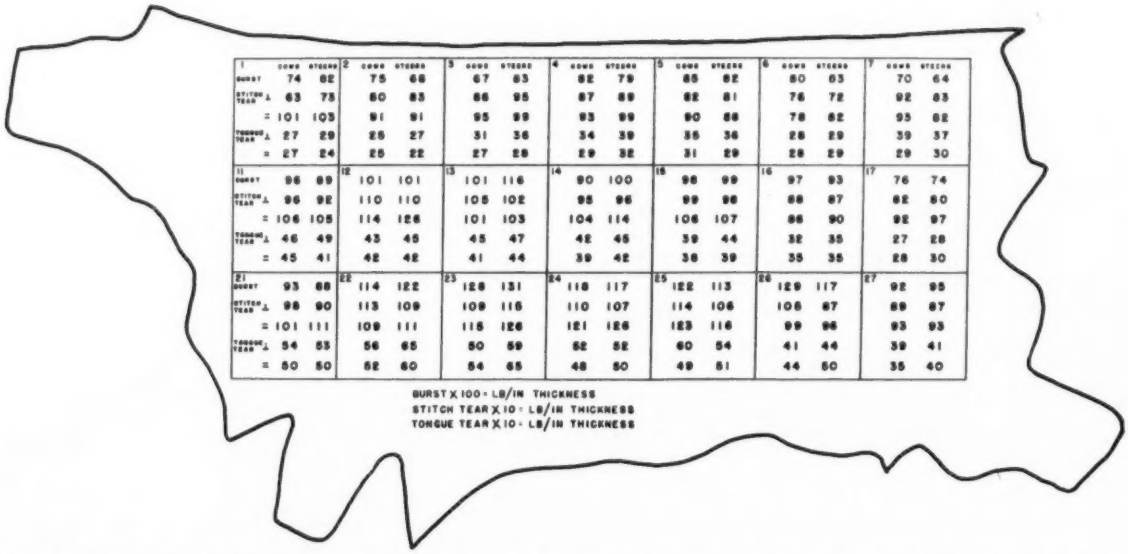
A comparison of the average values for the blocks of cow sides and steer sides, for thickness, tensile strength in two directions, and stretch at break in two directions, is given in Figure 2. The thickness values of the blocks for cows and steers are highly uniform and about the same for both types of sides. Tensile strength is generally highest in blocks taken from the belly locations, and it is in general higher in the parallel direction than in the perpendicular direction. This is similar to the results obtained with the split and unsplit chrome tanned sides. Stretch, on the average, is greater in the perpendicular direction than in the parallel direction and is greater for cow sides than for steer sides.

Block averages for burst and for stitch tear and tongue tear in two directions of test, for cows and steers, are given in Figure 3. Stitch tear, as in the case of tensile strength, is in general higher in the parallel direction than in the perpendicular direction. Tongue tear, on the other hand, is in general slightly greater in the perpendicular direction. In many blocks, as a rule of thumb, tongue tear strength can be considered as approximately one-half the corresponding stitch tear strength. As in the tensile strength tests, the greatest strengths for both tests are generally found in the belly locations. Bursting strength appears to correlate with other strength tests in that the values are greatest in the belly area and lowest in the butt and backbone areas.



	COWS	STEERS		COWS	STEERS		COWS	STEERS		COWS	STEERS		COWS	STEERS		COWS	STEERS		COWS	STEERS
1 THK	90	90	2 THK	89	89	3 THK	88	89	4 THK	91	92	5 THK	94	94	6 THK	95	95	7 THK	96	96
TENSILE △	199	192	TENSILE △	259	228	TENSILE △	291	269	TENSILE △	272	256	TENSILE △	268	267	TENSILE △	259	234	TENSILE △	321	299
=	349	375	=	343	331	=	348	316	=	372	373	=	432	415	=	351	341	=	256	226
STRETCH △	47	46	STRETCH △	47	47	STRETCH △	46	43	STRETCH △	56	52	STRETCH △	60	58	STRETCH △	56	53	STRETCH △	56	55
=	36	30	=	40	34	=	49	48	=	56	55	=	57	52	=	56	52	=	53	49
11 THK	86	86	12 THK	87	87	13 THK	93	93	14 THK	94	94	15 THK	94	94	16 THK	96	96	17 THK	93	95
TENSILE △	312	279	TENSILE △	409	358	TENSILE △	398	385	TENSILE △	339	327	TENSILE △	350	323	TENSILE △	348	313	TENSILE △	340	306
=	284	302	=	420	388	=	460	410	=	425	410	=	471	416	=	370	332	=	362	318
STRETCH △	50	47	STRETCH △	46	43	STRETCH △	51	48	STRETCH △	63	60	STRETCH △	61	59	STRETCH △	58	51	STRETCH △	58	50
=	42	34	=	43	37	=	58	53	=	56	58	=	57	52	=	60	52	=	57	53
21 THK	92	90	22 THK	89	88	23 THK	93	91	24 THK	93	90	25 THK	90	90	26 THK	88	89	27 THK	92	94
TENSILE △	356	286	TENSILE △	462	344	TENSILE △	483	411	TENSILE △	406	343	TENSILE △	440	343	TENSILE △	344	301	TENSILE △	324	282
=	308	187	=	416	408	=	524	350	=	584	417	=	599	437	=	437	310	=	341	314
STRETCH △	53	52	STRETCH △	58	57	STRETCH △	64	57	STRETCH △	66	62	STRETCH △	69	62	STRETCH △	55	49	STRETCH △	65	64
=	60	59	=	48	40	=	58	50	=	48	40	=	47	43	=	47	38	=	50	48

FIGURE 2.—Average values for thickness, tensile strength, and stretch in the different blocks of the sides.



	COWS	STEERS
1 BURST	74	82
STITCH TEAR Δ	63	75
=	101	103
TONGUE TEAR Δ	27	29
=	27	24
2 BURST	75	68
STITCH TEAR Δ	80	83
=	91	91
TONGUE TEAR Δ	25	27
=	25	22
3 BURST	67	83
STITCH TEAR Δ	86	95
=	95	99
TONGUE TEAR Δ	31	36
=	27	28
4 BURST	82	79
STITCH TEAR Δ	87	89
=	93	99
TONGUE TEAR Δ	34	39
=	29	32
5 BURST	85	82
STITCH TEAR Δ	82	81
=	90	86
TONGUE TEAR Δ	35	36
=	31	29
6 BURST	80	83
STITCH TEAR Δ	76	72
=	78	82
TONGUE TEAR Δ	28	29
=	28	29
7 BURST	70	64
STITCH TEAR Δ	92	83
=	93	82
TONGUE TEAR Δ	39	37
=	29	30
11 BURST	96	89
STITCH TEAR Δ	96	92
=	106	105
TONGUE TEAR Δ	46	49
=	45	41
12 BURST	101	101
STITCH TEAR Δ	110	110
=	114	126
TONGUE TEAR Δ	43	45
=	42	42
13 BURST	101	116
STITCH TEAR Δ	105	102
=	101	103
TONGUE TEAR Δ	45	47
=	41	44
14 BURST	90	100
STITCH TEAR Δ	95	96
=	104	114
TONGUE TEAR Δ	42	45
=	39	42
15 BURST	98	99
STITCH TEAR Δ	99	98
=	106	107
TONGUE TEAR Δ	39	44
=	38	39
16 BURST	97	93
STITCH TEAR Δ	88	87
=	86	90
TONGUE TEAR Δ	32	35
=	35	35
17 BURST	76	74
STITCH TEAR Δ	82	80
=	92	97
TONGUE TEAR Δ	27	28
=	28	30
21 BURST	93	88
STITCH TEAR Δ	98	90
=	101	111
TONGUE TEAR Δ	54	53
=	50	50
22 BURST	114	122
STITCH TEAR Δ	113	109
=	109	111
TONGUE TEAR Δ	56	65
=	52	60
23 BURST	128	131
STITCH TEAR Δ	109	115
=	115	126
TONGUE TEAR Δ	50	59
=	54	65
24 BURST	118	117
STITCH TEAR Δ	110	107
=	121	126
TONGUE TEAR Δ	52	52
=	48	50
25 BURST	122	113
STITCH TEAR Δ	114	106
=	123	116
TONGUE TEAR Δ	60	54
=	49	51
26 BURST	129	117
STITCH TEAR Δ	108	87
=	99	96
TONGUE TEAR Δ	41	44
=	44	50
27 BURST	92	95
STITCH TEAR Δ	89	87
=	93	93
TONGUE TEAR Δ	39	41
=	35	40

FIGURE 3.—Average value for bursting strength, stitch tearing strength, and tongue tearing strength in the different blocks of the sides.

The individual side averages for all of the physical tests made on the cow and steer sides are given in Table 2. A comparison of the differences in the results of the tests between the two sets of sides is shown in Table 3, where a position to position comparison is given. Only for tensile strengths where the differences are in the order of 11.3 and 13.2 per cent are the differences highly significant. The cow sides have the greater tensile strength. The difference between the two sets of sides in tongue tear is possibly real, the steer sides being slightly higher in tongue tear than the cow sides. Results for stitch tear and burst between the two sets of sides are not significantly different.

TABLE 3

Differences Between Values for Physical Properties Obtained for Cow and Steer Sides

(Results for Cow Sides Minus Results for Steer Sides)

Position	Tensile Strength 10 lb/in.²		Stitch Tearing Strength 10 lb/in. thickness		Tongue Tearing Strength 10 lb/in. thickness		Bursting Strength 10 lb/in. thickness
	⊥	//	⊥	//	⊥	//	
1	+ 7	−26	−10	− 2	−2	+ 3	− 8
2	+31	+12	− 3	0	−2	+ 3	+ 7
3	+ 2	+32	− 9	− 4	−4	− 1	−16
4	+16	− 1	− 2	− 6	−5	− 3	+ 3
5	+21	+19	+ 1	+ 2	−1	+ 2	+ 3
6	+25	+10	+ 4	− 4	−1	− 1	− 3
7	+22	+30	+ 9	+11	+2	− 1	+ 6
11	+33	−18	+ 4	+ 1	−3	+ 4	+ 7
12	+51	+65	0	−12	−1	0	0
13	+13	+50	+ 3	− 2	−2	− 3	−15
14	+12	+15	− 1	−10	−3	− 3	−10
15	+27	+55	+ 1	− 1	−5	− 1	− 1
16	+35	+38	+ 1	− 4	−3	0	+ 4
17	+34	+46	+ 2	− 5	−1	− 2	+ 2
21	+72	+121	+ 8	−10	+1	0	+ 5
22	+118	+11	+ 4	− 2	−9	− 8	− 8
23	+42	+174	− 6	+11	−9	−11	− 3
24	+63	+167	+ 3	− 5	0	− 2	+ 1
25	+97	+162	+ 8	+7	+5	− 2	+ 9
26	+43	+127	+18	+3	−3	− 6	+12
27	+42	+27	+ 2	0	−2	− 5	− 3
Average	+38	+53	+1.8	−1.5	−2.3	−1.8	−0.4
Percentage Difference	11.3	13.2	1.9	1.5	5.3	4.4	0.4

Coefficients of variation between sides for properties measured on corresponding blocks are given in Table 4. These results vary from 7 to over 30

TABLE 4

Coefficient of Variation of Physical Properties of Cow and Steer Sides
(Classification by blocks)

	Tensile Strength					Stitch Tearing Strength					Tongue Tearing Strength					Bursting Strength		
	⊥		∥			⊥		∥			⊥		∥					
Block	Cow Sides %	Steer Sides %	Cow Sides %	Steer Sides %	Avg. %	Cow Sides %	Steer Sides %	Cow Sides %	Steer Sides %	Avg. %	Cow Sides %	Steer Sides %	Cow Sides %	Steer Sides %	Avg. %	Cow Sides %	Steer Sides %	Avg. %
1	18	15	12	13	15	17	35	16	18	22	27	29	28	24	27	15	18	16
2	19	15	22	12	17	17	23	14	16	18	22	40	24	33	30	25	20	22
3	14	16	9	13	13	16	14	9	10	12	21	30	25	16	23	10	17	14
4	18	25	19	14	19	12	22	9	7	13	22	19	20	12	18	13	10	12
5	13	15	12	11	13	17	15	10	9	13	15	24	14	18	18	18	14	16
6	15	21	17	14	17	11	9	9	12	10	10	26	15	18	17	14	14	14
7	17	16	16	17	17	11	15	12	15	13	18	23	21	21	21	15	24	14
11	11	13	28	20	18	13	21	11	22	20	22	25	20	26	23	9	14	12
12	11	11	20	22	16	7	18	11	14	12	26	28	21	18	23	18	27	22
13	12	10	14	15	13	12	11	11	12	12	14	14	16	22	16	15	13	14
14	17	16	12	15	15	22	12	7	14	14	17	16	16	16	16	20	10	15
15	14	12	14	17	14	11	10	10	11	10	17	14	14	14	15	16	16	16
16	12	15	15	12	14	8	13	11	13	11	15	23	15	16	17	11	15	13
17	14	14	12	14	14	20	12	18	15	16	17	28	13	18	19	23	19	21
21	9	19	35	34	24	9	28	19	14	18	21	25	20	26	23	24	16	20
22	8	20	18	10	14	10	12	19	12	13	13	18	19	31	20	11	12	12
23	8	10	12	23	13	9	12	7	12	10	12	21	11	9	13	12	12	12
24	11	16	12	18	14	12	15	10	12	12	12	22	14	18	16	9	8	8
25	9	20	9	20	15	9	13	9	12	8	12	23	8	22	16	9	12	10
26	11	19	17	24	18	15	23	13	18	17	13	21	19	17	18	14	15	14
27	22	17	19	16	19	17	15	14	14	15	13	20	14	23	18	22	12	17
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Avg.	13	16	16	17		13	17	12	13		17	23	17	20		15	15	

per cent. The properties determined are slightly less variable for the cow sides than for the steer sides on the average, except for burst which is the same for both.

The average coefficients of variation for each physical property for cow sides and steer sides lumped together, are shown in Figure 4. This figure shows that the properties determined on the blocks in the middle of the sides are, in general, the least variable; for example, blocks 6, 14, 15, and 23. Those blocks on the ends of the sides, in all cases, show the greatest variability.

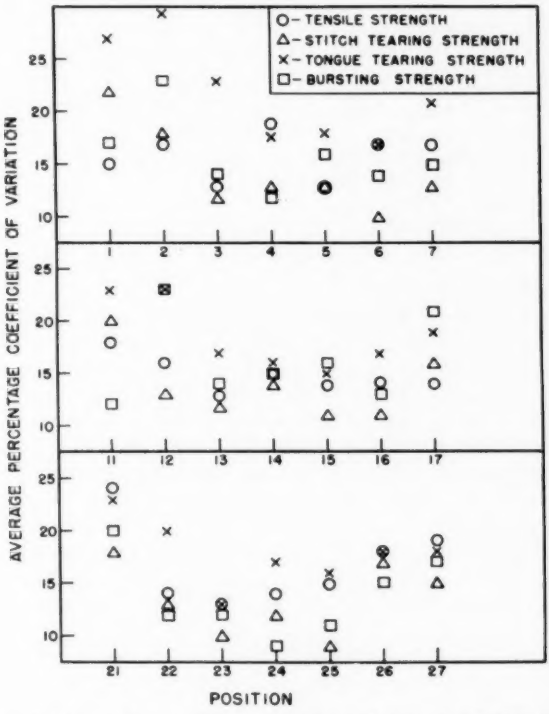


FIGURE 4.—Relation of the average percentage coefficient of variation for the four physical tests to positions on the side for chrome-retanned cow and steer sides.

Coefficients of variation between side averages for tensile strength, stitch tearing strength, tongue tearing strength, and bursting strength are given in Table 5. Cow sides show less variability than the steer sides in all but the

tests on stitch tear in the parallel direction and the bursting test. This is similar to the findings given in Table 4 where the comparison of the variability between corresponding blocks is given.

TABLE 5

Coefficients of Variation of Side Averages for Various Physical Properties of Cow and Steer Sides

Test	c. of v. for Cow Sides %	c. of v. for Steer Sides %
Tensile strength:		
Perpendicular	8.8	10.0
Parallel	9.1	11.0
Stitch tear strength:		
Perpendicular	6.8	8.2
Parallel	9.8	5.1
Tongue tear strength:		
Perpendicular	8.8	10.5
Parallel	7.3	9.0
Burst	9.4	7.4

4.2 *Water Resistance*

Results of the water resistance properties for the cow and steer sides are given in Figure 5 as averages for various blocks of the hide for those on which measurements were made. The averages were obtained from values for six or seven individual measurements of the water vapor permeability, the penetration point in flexes or the point at which the first drop of water penetrates the leather, the amount of water absorbed by the leather, and the amount of water absorbed by the wick. The last test is made by placing a wick in the cup formed by the leather when clamped in the machine and flexing the leather for 15 minutes.

Correlation coefficients for some of the water resistance relationships are given in Table 6. Water vapor permeability shows a high negative correlation with grease content of steer sides; see Figure 6. The other correlations of the water resistance relationships are too small to be of practical significance. A graph is shown in Figure 7 which gives the penetration time in relation to the wick pickup for the cow sides. In general, the variability of the data relating to water resistance properties is so large as to render their practical value questionable.

4.3 *Results of Chemical Tests*

The results of the chemical tests on the cow and steer sides are given as block averages in Figure 8. Since it was observed in the study of the split and unsplit leathers that reliable values for chemical analysis could be ob-

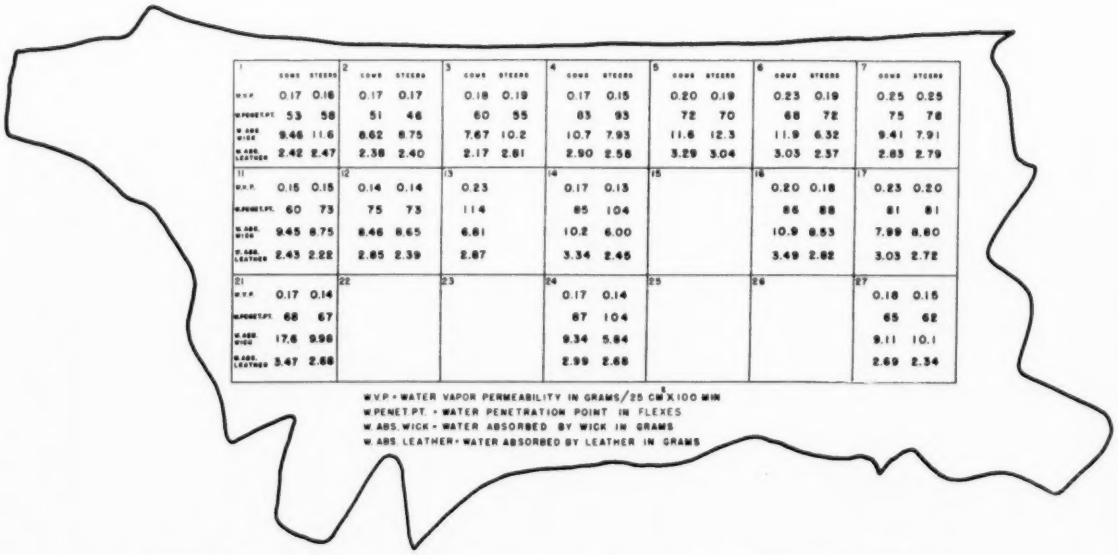


FIGURE 5.—Average values for the water resistance properties in the different blocks of the sides.

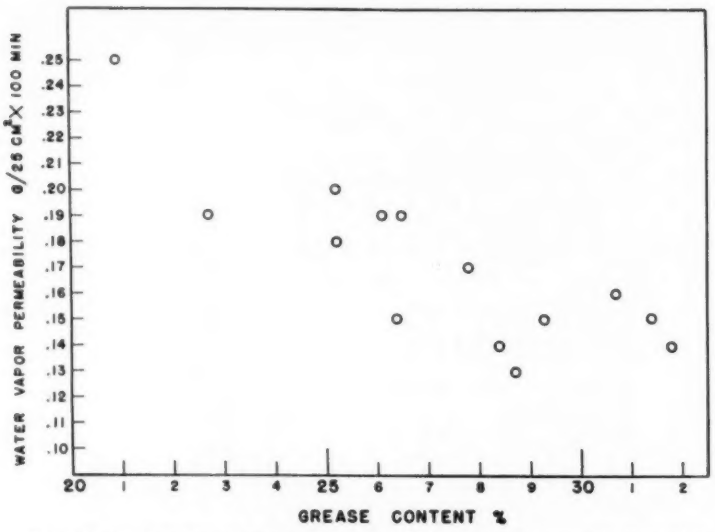


FIGURE 6.—Relation of water vapor permeability to grease content of steer sides.

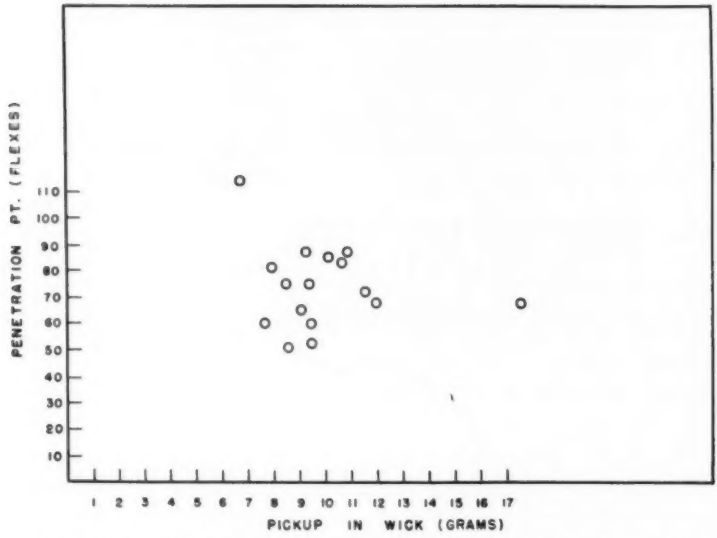


FIGURE 7.—Relation of point of penetration to pickup in wick for the cow sides.

TABLE 6

Correlation Coefficients for Various Water Resistance Relationships

	c. c. for Cows	c. c. for Steers
Water vapor permeability versus grease contents	−0.66	−0.83
Penetration time versus wick pickup	−0.18	−0.67
Pickup in leather versus wick pickup	0.59	0.29
Wick pickup versus grease content	0.17	0.19
Leather pickup versus grease content	−0.14	−0.31

tained with a few hides, only four cow sides and four steer sides were used in these tests. It may be observed that the grease variation is about 50 per cent between block 7 and block 21, which is usually the maximum variation for the side.

The results of the chemical tests and calculations made therefrom are given in Tables 7 and 8. The calculations shown in this table indicate that the ratio of moisture and chrome content to the hide substance is approximately the same for all blocks. An even less variable relation is obtained for the relative quantity of moisture held in the combined hide substance and tannin. The chrome is present in a definite ratio to the hide substance in all blocks, as was also shown for the split and unsplit chrome tanned leather. The grease varies in inverse proportion to the hide substance, as was the case for the split and unsplit leathers. The relation of the hide substance with the moisture, chromic oxide, and grease for cow sides is shown in Figures 9, 10, and 11, respectively.

Since the cow and steer sides are retanned with vegetable tannins, an additional variable in composition is introduced. This is further complicated by the fact that there is no direct method of determining vegetable tannin in leather. The procedure tried and found satisfactory with the split and unsplit chrome tanned leathers for determining total composition may be applied to the cow and steer sides. Tables 7 and 8 give the results obtained for vegetable tannin by difference after making these calculations, namely: adding values for hide substance, grease, 2.73 x Cr_2O_3 content, and ash - Cr_2O_3. The difference between the totals of these values and 100 gives the tannin content in per cent.

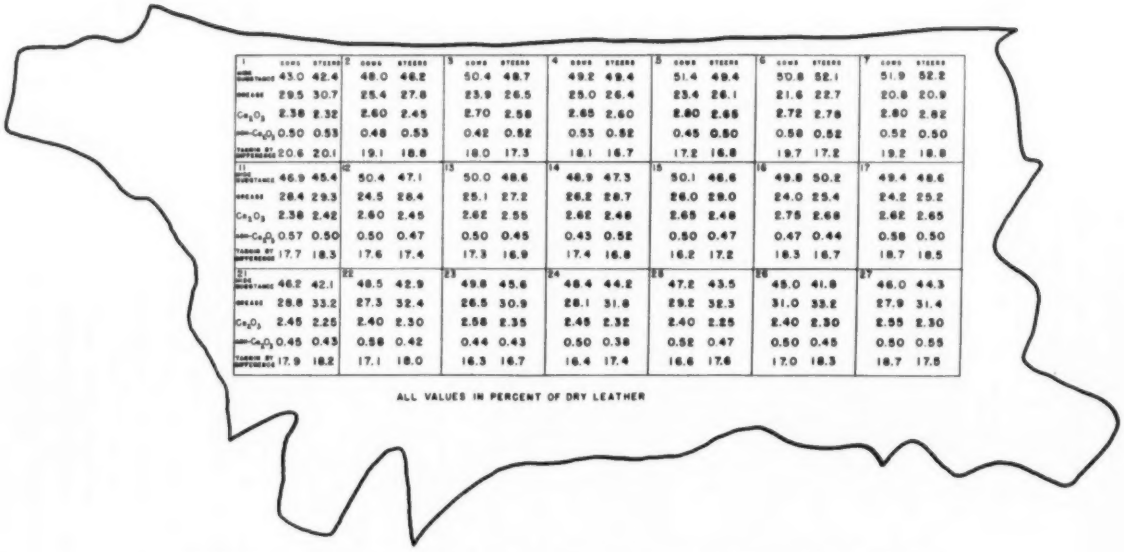


FIGURE 8.—Average values for the chemical constituents in the different blocks of the sides.

TABLE 7

Chemical Analysis (Cow Sides)

	1	2	3	4	5	6	7	8	9	10	11	12		
							Moisture		Cr_2O_3					
Block	Hide Substance %	Chromic Oxide Cr_2O_3 %	Ash %	Grease %	Moisture %	pH	Hide Substance	Hide Substance + tannin	Hide Substance	Ash-Cr_2O_3 %	2.73 x Cr_2O_3 %	Hide Substance x grease	Analysis sum % 1+4+10+11	Vegetable tannin = 100% - Analysis sum
1	43.0	2.39	2.88	29.5	10.5	3.0	0.244	0.165	0.055	0.50	6.50	0.127	79.5	20.5
2	48.0	2.60	3.08	25.4	11.2	3.0	0.233	0.167	0.054	0.48	7.10	0.122	81.0	19.0
3	50.4	2.70	3.12	23.9	11.4	3.0	0.226	0.167	0.054	0.42	7.37	0.120	82.1	17.9
4	49.2	2.65	3.18	25.0	11.4	3.0	0.232	0.169	0.054	0.53	7.23	0.123	82.0	18.0
5	51.4	2.80	3.25	23.4	11.5	3.0	0.224	0.168	0.054	0.45	7.64	0.120	82.9	17.1
6	50.8	2.72	3.30	21.6	11.8	3.0	0.232	0.167	0.054	0.58	7.43	0.109	80.4	19.6
7	51.9	2.80	3.32	20.8	11.9	3.1	0.229	0.167	0.054	0.52	7.64	0.108	80.9	19.1
11	46.9	2.38	2.95	28.4	10.6	3.0	0.226	0.164	0.051	0.57	6.50	0.133	82.4	17.6
12	50.4	2.60	3.10	24.5	11.2	3.0	0.222	0.165	0.052	0.50	7.10	0.123	82.5	17.5
13	50.0	2.62	3.12	25.1	11.3	3.0	0.226	0.168	0.052	0.50	7.15	0.126	82.8	17.3
14	48.9	2.62	3.05	26.2	11.0	3.0	0.225	0.165	0.054	0.43	7.15	0.128	82.7	17.3
15	50.1	2.65	3.15	26.0	11.2	3.0	0.224	0.169	0.053	0.50	7.23	0.130	83.8	16.2
16	49.8	2.75	3.22	24.0	11.3	3.1	0.227	0.166	0.055	0.47	7.51	0.120	81.8	18.2
17	49.4	2.62	3.20	24.2	11.3	3.1	0.229	0.166	0.053	0.58	7.15	0.120	81.3	18.7
21	46.2	2.45	2.90	28.8	10.4	3.1	0.225	0.162	0.053	0.45	6.69	0.133	82.1	17.9
22	48.5	2.40	2.98	27.3	10.8	3.0	0.223	0.165	0.049	0.58	6.55	0.132	82.9	17.1
23	49.8	2.58	3.02	26.5	11.0	3.0	0.221	0.166	0.052	0.44	7.04	0.132	83.8	16.2
24	48.4	2.45	2.95	28.1	10.4	3.0	0.215	0.166	0.051	0.50	6.69	0.136	83.7	16.3
25	47.2	2.40	2.92	29.2	10.7	3.1	0.227	0.168	0.051	0.52	6.55	0.138	83.5	16.5
26	45.0	2.40	2.90	31.0	9.9	3.0	0.220	0.160	0.053	0.50	6.55	0.140	83.0	17.0
27	46.0	2.55	3.05	27.9	10.9	3.1	0.237	0.168	0.055	0.50	6.96	0.128	81.4	18.6

TABLE 8

Chemical Analysis (Steer Sides)

	1	2	3	4	5	6	7	8	9	10	11	12		
							Moisture		Cr_2O_3					
Block	Hide Substance %	Chromic Oxide Cr_2O_3 %	Ash %	Grease %	Moisture %	pH	Hide Substance	Hide Substance + tannin	Hide Substance	Ash-Cr_2O_3 %	2.73 x Cr_2O_3 %	Hide Substance x grease	Analysis sum % 1+4+10+11	Vegetable tannin = 100% − Analysis sum
1	42.4	2.32	2.85	30.7	10.4	3.0	0.245	0.166	0.055	0.53	6.33	0.130	80.0	20.0
2	46.2	2.45	2.98	27.8	10.9	3.0	0.236	0.168	0.053	0.53	6.69	0.128	81.2	18.8
3	48.7	2.58	3.10	26.5	11.2	3.0	0.230	0.170	0.053	0.52	7.04	0.129	82.8	17.2
4	49.4	2.60	3.12	26.4	11.2	3.0	0.227	0.170	0.053	0.52	7.10	0.130	83.4	16.6
5	49.4	2.65	3.15	26.1	11.2	3.0	0.227	0.169	0.054	0.50	7.23	0.129	83.2	16.8
6	52.1	2.78	3.30	22.7	11.7	3.0	0.225	0.169	0.053	0.52	7.59	0.118	82.9	17.1
7	52.2	2.82	3.32	20.9	11.8	3.0	0.226	0.164	0.054	0.50	7.70	0.109	81.3	18.7
11	45.4	2.42	2.92	29.3	10.5	3.0	0.231	0.165	0.053	0.50	6.61	0.133	81.8	18.2
12	47.1	2.45	2.92	28.4	10.7	3.0	0.227	0.166	0.052	0.47	6.69	0.134	82.7	17.3
13	48.6	2.55	3.00	27.2	10.9	3.0	0.223	0.167	0.052	0.45	6.96	0.132	83.2	16.8
14	47.3	2.48	3.00	28.7	10.6	3.0	0.223	0.165	0.052	0.52	6.77	0.136	83.3	16.7
15	46.6	2.48	2.95	29.0	10.5	3.0	0.225	0.164	0.053	0.47	6.77	0.135	82.8	17.2
16	50.2	2.68	3.12	25.4	11.2	3.0	0.223	0.167	0.053	0.44	7.32	0.128	83.4	16.6
17	48.6	2.65	3.15	25.2	11.1	3.0	0.228	0.165	0.055	0.50	7.23	0.122	81.5	18.5
21	42.1	2.25	2.68	33.2	9.7	3.0	0.230	0.161	0.053	0.43	6.14	0.140	81.9	18.1
22	42.9	2.30	2.72	32.4	10.0	3.0	0.233	0.164	0.054	0.42	6.28	0.139	82.0	18.0
23	45.6	2.35	2.78	30.9	10.2	3.0	0.224	0.164	0.052	0.43	6.42	0.141	83.4	16.6
24	44.2	2.32	2.70	31.8	9.8	3.0	0.222	0.159	0.052	0.38	6.33	0.141	82.7	17.3
25	43.5	2.25	2.72	32.3	9.7	3.0	0.223	0.159	0.052	0.47	6.14	0.141	82.4	17.6
26	41.8	2.30	2.75	33.2	9.4	3.0	0.225	0.156	0.055	0.45	6.28	0.139	81.7	18.3
27	44.3	2.30	2.85	31.4	9.9	3.0	0.223	0.160	0.052	0.55	6.28	0.139	82.5	17.5

TABLE 9

Coefficients of Variation of Grease, Hide Substance, and Chromic Oxide Between Sides on Corresponding Blocks for Cow and Steer Sides

Location	Grease		Hide Substance		Chromic Oxide	
	c. v. for Cow %	c. v. for Steer %	c. v. for Cow %	c. v. for Steer %	c. v. for Cow %	c. v. for Steer %
1	7.1	10.7	5.8	6.6	5.5	4.3
2	9.1	8.3	5.6	3.5	5.4	2.4
3	3.8	4.2	3.6	2.9	3.0	1.9
4	6.4	5.7	4.9	2.4	4.9	3.1
5	6.4	6.5	5.4	3.4	4.3	2.3
6	6.9	6.6	7.3	4.6	6.2	1.8
7	8.2	7.2	3.9	2.7	2.9	3.5
11	6.7	7.8	3.4	4.4	7.1	5.4
12	12.2	7.7	6.7	3.6	6.9	5.3
13	6.4	9.9	4.6	4.9	5.0	5.1
14	8.4	9.8	5.9	4.7	7.3	4.0
15	11.5	9.7	6.8	6.0	6.4	4.0
16	7.9	11.8	5.2	4.4	3.6	3.7
17	6.6	8.3	3.8	3.7	5.0	3.8
21	5.2	13.3	4.5	8.3	2.4	7.6
22	5.2	10.5	3.7	6.3	3.3	5.2
23	8.3	10.4	5.4	5.0	3.9	5.5
24	5.0	9.1	4.3	5.9	4.1	4.3
25	5.8	5.9	4.4	4.6	3.3	2.7
26	4.8	6.9	2.9	5.7	5.0	6.1
27	6.8	6.4	4.6	3.2	2.4	9.6

Coefficients of variation between sides on corresponding blocks for grease, hide substance, and chromic oxide are given in Table 9. Similar results for side averages are given in Table 10. The variability of the results is seen to be of the same order of magnitude for steer and cow sides, in each of the three properties. The grease content for both sets is more variable than that of either the hide substance or the chromic oxide.

TABLE 10

Coefficients of Variation of Grease, Hide Substance and Chromic Oxide Between Side Averages for Cow and Steer Sides

	Grease	Hide Substance	Cr_2O_3
C. of V. for Cow Sides, %	6.3	4.4	3.7
C. of V. for Steer Sides, %	7.1	3.0	3.4

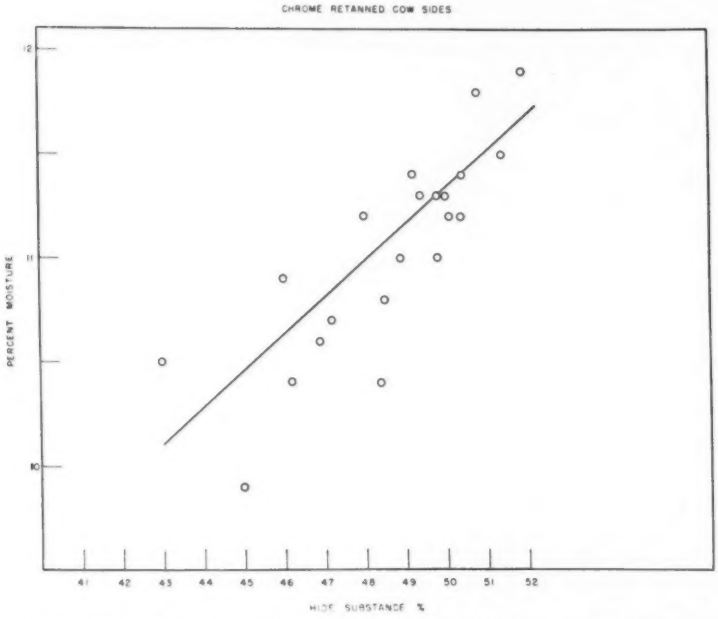


FIGURE 9.—Relation of moisture content to hide substance content for cow sides.

TABLE 11

Comparison of the Strength of Chrome and Chrome-retanned Leathers
(Average for all sides)

	Chrome-tanned		Chrome-retanned	
	Split	Unsplit	Cows	Steers
Tensile strength, 10 lb/in²				
Perpendicular	416	418	341	303
Parallel	502	506	402	349
Stitch tearing strength, 10 lb/ in thickness				
Perpendicular	126	121	94	93
Parallel	140	131	102	103
Tongue tearing strength, 10 lb/in thickness				
Perpendicular	68	67	40	43
Parallel	63	66	37	40
Bursting strength, 100 lb/ in thickness	140	133	99	99

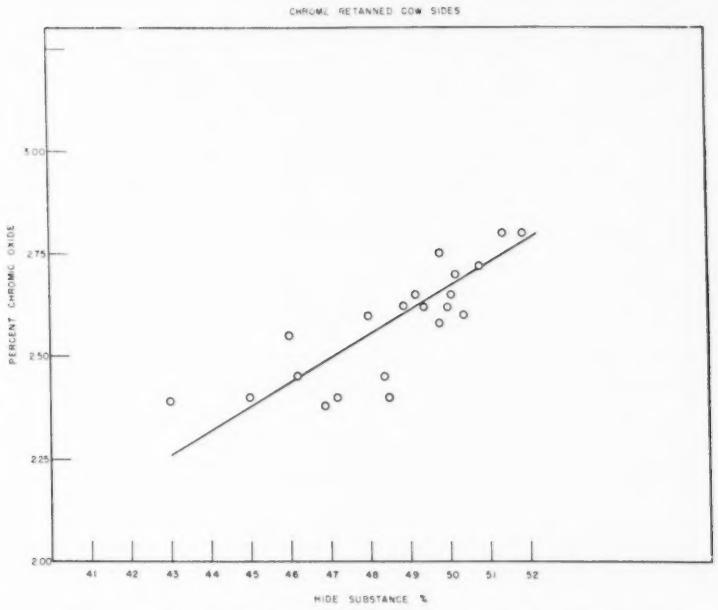


FIGURE 10.—Relation of chromic oxide to hide substance content for cow sides.

5. Comparison of Chrome and Chrome-Retanned Leather

Sufficient information is now available on chrome and chrome-retanned side leather to permit some definite statements in regard to their comparative physical properties:

(a) Chrome-retanned leathers are about 25 per cent weaker in tensile strength, stitch tearing strength, and burst than chrome-tanned leathers, and about 40 per cent weaker in tongue tearing strength. (Table II).

(b) Chrome-retanned leathers are less resistant to the penetration of water and water vapor than chrome-tanned leathers. (Table 12).

(c) Chrome-retanned leathers have a less variable grease content than chrome-tanned leathers. The grease content varies from 21 to 33 per cent over the area of the hide for the former and 20 to 45 per cent for the latter. (Table 13).

(d) Chrome-tanned leathers show considerably more stretch at the breaking point than chrome-retanned leathers. (Table 14).

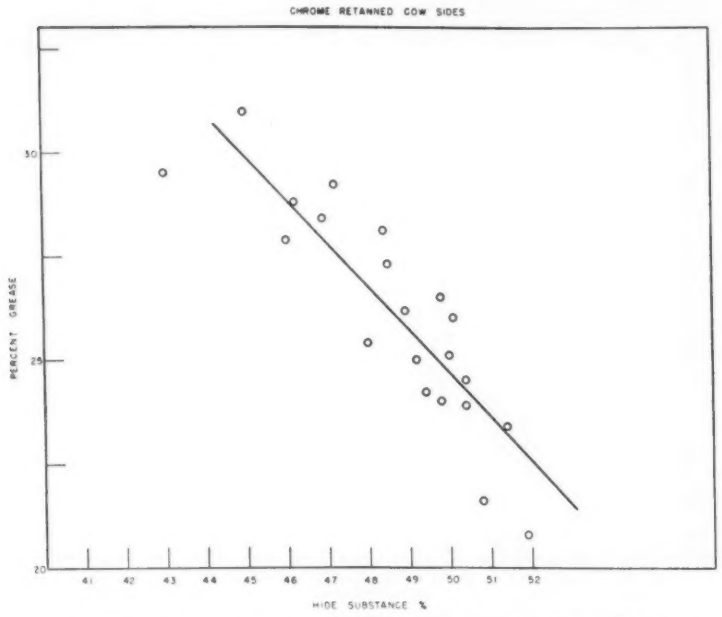


FIGURE 11.—Relation of grease to hide substance content for cow sides.

TABLE 12

Comparison of the Water Vapor Permeability and Water Penetration of Chrome and Chrome-Retanned Leathers

(Water vapor permeability in grams/25cm² x 100 min)
(Water penetration in grams absorbed by wick)

Position	Water vapor permeability				Water penetration			
	Chrome-tanned leather		Chrome-retanned leather		Chrome-tanned leather		Chrome-retanned leather	
	Split	Unsplit	Cows	Steers	Split	Unsplit	Cows	Steers
1	0.05	0.02	0.17	0.16	8.3	7.3	9.5	11.6
2	0.05	0.03	0.17	0.17	7.3	4.4	8.6	8.8
3	0.06	0.04	0.18	0.19	9.9	5.8	7.7	10.2
4	0.07	0.03	0.17	0.15	8.1	4.7	10.7	7.9
5	0.07	0.05	0.20	0.19	6.5	5.4	11.6	12.3
6	0.09	0.04	0.23	0.19	7.0	6.1	11.9	36.
7	0.12	0.06	0.25	0.25	5.8	4.9	9.4	7.9
11	0.03	0.02	0.15	0.15	5.3	3.2	9.4	8.8
12	0.04	0.03	0.14	0.11	5.6	2.5	8.5	8.7
13	0.04	0.02	0.23		5.1	2.2	6.8	

TABLE 12 (Continued)

Position	Water vapor permeability				Water penetration			
	Chrome-tanned leather		Chrome-retanned leather		Chrome-tanned leather		Chrome-retanned leather	
	Split	Unsplit	Cows	Steers	Split	Unsplit	Cows	Steers
14	0.06	0.04	0.17	0.13	4.2	4.4	10.2	6.0
15	0.06	0.03			3.8	2.6		
16	0.08	0.05	0.20	0.18	2.9	3.0	10.9	8.5
17	0.12	0.05	0.23	0.20	4.9	5.0	8.0	8.8
21	0.03	0.02	0.17	0.14	2.5	1.4	17.6	10.0
22	0.04	0.03			3.1	1.5		
23	0.03	0.03			2.6	2.2		
24	0.05	0.03	0.17	0.14	3.8	2.4	9.3	5.8
25	0.06	0.04			2.8	3.4		
26	0.04	0.03			4.0	2.7		
27	0.06	0.03	0.18	0.15	6.4	6.7	9.1	10.1

TABLE 13

Comparison of the Grease Contents of Chrome and Chrome-Retanned Leathers

Positions	Grease content of Chrome-tanned leather		Grease content of Chrome-retanned leather	
	Split %	Unsplit %	Cows %	Steers %
1	35.4	35.4	29.5	30.7
2	33.0	33.6	25.4	27.8
3	27.6	27.4	23.9	26.5
4	26.4	24.2	25.0	26.4
5	25.0	22.2	23.4	26.1
6	24.7	21.0	21.6	22.7
7	22.5	20.4	20.8	20.9
11	36.4	38.9	28.4	29.3
12	33.9	35.4	24.5	28.4
13	29.5	29.6	25.1	27.2
14	27.0	26.7	26.2	28.7
15	27.0	25.7	26.0	29.0
16	25.2	22.1	24.0	25.4
17	26.1	23.7	24.2	25.2
21	44.6	44.9	28.8	33.2
22	44.0	44.8	27.3	32.4
23	36.8	38.3	26.5	30.9
24	30.3	33.0	28.1	31.8
25	30.2	32.7	29.2	32.3
26	38.2	40.9	31.0	33.2
27	33.4	37.0	27.9	31.4

TABLE 14

Comparison of the Stretch of Chrome-Tanned and Chrome-Retanned Leathers

Position	Stretch of Chrome-tanned leather				Stretch of Chrome-retanned leather			
	Split		Unsplit		Cows		Steers	
	⊥ %	∥ %	⊥ %	∥ %	⊥ %	∥ %	⊥ %	∥ %
1	79	40	85	39	67	36	66	30
2	61	44	66	43	47	40	47	34
3	60	52	62	50	46	49	43	45
4	69	60	63	59	56	56	52	55
5	72	56	66	53	60	57	58	52
6	66	62	61	55	56	56	53	52
7	61	67	58	62	56	53	55	49
11	62	39	57	40	50	42	47	34
12	56	42	57	44	46	43	43	37
13	56	53	53	50	51	58	48	53
14	64	59	57	61	63	56	60	55
15	63	56	57	54	61	57	59	52
16	58	60	51	56	58	60	51	52
17	65	60	58	53	58	57	50	53
21	65	67	58	65	53	60	52	59
22	69	44	68	44	58	46	57	40
23	63	55	64	49	64	56	57	50
24	67	47	71	46	66	48	62	40
25	70	47	81	46	69	47	62	43
26	63	63	77	63	55	47	49	38
27	65	51	68	60	65	50	64	48

The vegetable tannins apparently tend to plump the flankier areas of the hide to produce a thicker and firmer leather. The filling of the spaces between the fibers by the tannins allows the leather to stretch less at the point of break. The hydrophilic character of the vegetable tannins makes the chrome-retanned leather less water resistant than the chrome tanned leather which is stuffed with higher percentages of grease.

6. References

1. C. W. Mann, E. B. Randall, John Mandel, T. J. Kilduff, and A. M. Charles, *J.A.L.C.A.* **46,** 248 (1951).
2. E. B. Randall, T. J. Carter, T. J. Killduff, C. W. Mann and J. R. Kanagy, *J.A.L.C.A.* **47,** 404 (1952).
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ABSTRACTS

Liming. I. Influence of Various Conditions of Liming on the Hydrolysis of Skin and Hair. By H. Toyoda, *Rept. Chem. Ind. Research Inst., Tokyo*, **46,** 55 (1951). Through *C. A.* **46,** 2323 (1952). Rabbit skin (corium) and hair were hydrolyzed in a saturated lime solution at a nearly uniform rate for days, as determined by the nitrogen dissolved. The hydrolysis was almost wholly unaffected by the volume of the solution and the concentration of the lime used. The addition of sodium sulfide to the lime solution accelerated the rate of hydrolysis of the hair markedly but that of the skin only slightly. The amount of the sample hydrolyzed was unrelated to the amount of sulfide added.

Liming. II. Change of the Distribution of Protein Nitrogen in Animal Skin by Liming. By H. Toyoda. *Repts. Govt. Chem. Ind. Research Inst.*, Tokyo, **46,** 62 (1951). Through *C. A.* **46,** 2324 (1952). Purified rabbit skin and fat free hair were kept in saturated calcium hydroxide solutions, with or without adding Na_2S at 25° for 1-20 days. After the liming, the amide and diamino nitrogen decreased and monoamino nitrogen increased in the collagen of the skin. The amide and monoamino nitrogen decreased and the diamino nitrogen increased in the keratin of the hair.

Shagreen of Shark Skin. I. Removal and Components of Shagreen. By E. Sugano. *Repts. Govt. Chem. Ind. Research Inst.*, Tokyo, **46,** 153 (1951). Through *C. A.* **46,** 2324 (1952). The shagreen of shark (Japanese species) skin was easily separated intact by dissolving the skin in a buffer solution with pancreatin or papain. Pepsin dissolved shagreen to some extent. The latter analyzed proteins 32.72, PO_4 42.19, Ca 24.46, Fe 0.55, and Mg 0.08 per cent.

Shagreen of Shark Skins. II. *Repts. Govt. Chem. Ind. Research Inst., Tokyo*, **46,** 157 (1951). Through *C. A.*, **46,** 2325 (1952). A large part of the shagreen was soluble in 5 *N* HCl or HNO_3, but only some proteins dissolved in saturated alkali solutions. In neutral salts it was adsorbed. All of the inorganic components dissolved in dilute HCl, but the proteins began to dissolve only in 3 *N* HCl at 30° or 5 *N* HCl at room temperature. Some proteins always remained intact. After tanning the skin with quebracho, chrome mordants or formaldehyde, the shagreen became less soluble in acids but more soluble after treating with aluminum chloride.

Adhesive Properties of Proteins I. Effects of Moisture and Temperature on the Adhesion and Mechanical Strength of Protein Films. By N. Shikazono. *Repts. Govt. Chem. Ind. Research Inst.*, Tokyo **45,** 119 (1950). Through *C. A.* **46,** 2325 (1952). The Adhesion F of gelatin and casein films painted on a glass or copper surface, as determined by stripping, was found to be related to the water content ∞ of the films (determined by drying at 100-100°) as $F = Ae^{-B\infty}$, where A and B are constants. The tensile strength varied parallel to F, and both decreased in summer and increased in winter.

Adhesive Properties of Proteins. II. Differences in Adhesion Among Proteins. By N. Shikazono. *Repts. Govt. Chem. Ind. Research Inst.*, Tokyo **45,** 127 (1959). Through *C. A.* **46,** 2325 (1952). Casein and gelatin which easily form films in solutions and are easily spun (with linear molecular arrangement) were more adhesive than soybean protein and egg albumin which were hard to draw into films in solutions and hard to spin (with spherical molecular arrangement).

Adhesive Properties of Proteins. III. Change of Adhesion of Proteins by Mild Hydrolysis. By N. Shikazono and H. Tsujiuchi. *Repts. Govt. Chem. Ind. Research Inst.*, Tokyo **45,** 134 (1950). Through *C. A.* **46,** 2325 (1952). Casein and gelatin hydrolyzed mildly with dilute acid or alkali, remained unaffected until the polymerization was reduced below a certain degree; with further hydrolysis they showed a decrease in adhesion but relative constancy in tensile strength.

Adhesive Property of Proteins. IV. Effects of Some Agents Added on the Adhesion of Proteins. By N. Shikazono and T. Ohara. *Repts. Govt. Chem. Ind. Research Inst.*, Tokyo, **45,** 138 (1950). Through *C. A.* **46,** 2325 (1952). The adhesion of gelatin on glass decreased when inorganic acid, PhOH, $OHC_6H_4SO_2OH$, or OHC_6H_4COOH was added (gelatin dissociated as a base), but increased when alkali was added (gelatin dissociated as an acid), and was no longer proportional to the tensile strength except qualitatively when the agent linked the polypeptide chains more firmly (e.g. Cr_2O_7, aldehydes, or a reducing agent). The simultaneous presence of $CuSO_4$ and NaOH increased the adhesion markedly, both effects above acting together.

Technological Properties of the Tannin PL. By K. V. Rykberg and S. V. Gerasev. *Legkaya Prom.* **11,** No. 2, 26 (1951). Through *C. A.* **46,** 3307 (1952). Tannin PL dissolves easily in water with a brownish pink color; it has no peptizing action. Leather tanned with oak + PL + AN (60:25:15) had a higher tannin content number and greater weight and thickness yields than with sulfite cellulose extract. Sole leather tanned with oak + PL or fir + PL (1:1) was unsatisfactory. However, with oak + fir + PL (50:15:35), the results were as good as with oak + AN (80:20). Equally good results with regard to weight and thickness were obtained with oak + fir + PL + AN (50:10:30:10). In tanning Russia leather, satisfactory results were obtained with oak + fir + PL (15:35:50 and 20:30:50) or oak + PL and fir + PL (1:1). The leather was of high organoleptic quality: very full, elastic, and without any shrinkage. Analysis showed grease 22.3, ash 4.8, total soluble matter 5, inorganic soluble matter 1.8, hide substance 49.8, combined tannins 19.9, tanning number 40, pH 5.5, Cr_2O_3 0.7, rupture resistance 2.95, elongation under load 20, hygrothermal stability 92.7, and water permeability 0.54 per cent, elasticity 500, and hardness 123. PL will make it possible to replace a large part of oak tannins.

Reaction of Gelatin with Plant Tannins. By A. G. Pasynskii and A. Popova. *Zhur. Priklad. Khim.* **24,** 1191 (1951). Through *C. A.* **46,** 3307 (1952). The deviation from additivity of potentiometric titration curves of mixtures of purified gelatin with tannin (Kahlbaum pure oak extract) is assumed to be a measure of the degree of interaction of the two substances. The value of deviation is minus at pH 4-5, that is at the isoelectric point. The deviation increases with acidification while in the alkaline range it reaches a maximum at about pH 8.5 – 9.5. At pH 10 the pure tannin binding amounted to 0.9 gram per gram gelatin, while at pH 6-8 it is 0.5 – 0.6 gram per gram. For oak extract at pH 6 it is 0.2 – 0.4 gram per gram. The isoelectric point of the protein is simultaneously shifted to pH 3.6 by tannin and to 4.4 by oak extract.

The Use of Waste Sulfite Liquor. By A. Majrich. *Chemie* (Prague) **5,** 3 (1949). Through *C. A.* **46,** 3272 (1952). The author describes attempts to use the lignin substances in the preparation of vanillin, hydrated phenols, resins, tanning agents, permutoids, adhesives, sizing substances, and highway materials. The fermentable substances lead to the production of ethyl alcohol.

The Problem of the Utilization of Domestic Sources of Tannin. By B. Mintchev, G. Pojarliev, K. Nicoltchev, and E. Marcov. *Rev. insts. recherches sci. ministeres agr. et forets, Ser. agron.* (Bulgaria) **18,** No. 2, 173 (1950). Through *C. A.* **46,** 2830 (1952). Seventy-nine samples of Bulgarian plants were analyzed for tannin and other constituents. Sumac *(Rhus. continus)* proved the most promising for the preparation of tannin for domestic use and export. Mixed sumac leaves and branches contained 17.2 per cent tannin while some leaves were as high as 23.5 per cent.

Aeaction Between Chrome Salts and Sulfite Cellulose Tannins. By S. A. Kuraitis, *Legkaya Prom.* **9,** No. 1, 16 (1949). Through *C. A.* **46,** 2831 (1952). Sulfite cellulose tannins expelled some of the chrome from leather after chrome tanning. Treatment with sulfonaphthenic acids prior to chrome tanning did not affect the process substantially; chrome was still expelled. Two cases are possible: entry of lignosulfonic acid into the chrome complex with the expulsion of a sulfate group and the simultaneous presence of lignosulfonate and sulfate groups. In both cases, the decrease in the tanning capacity of the chrome salts can be due to both a decrease of sulfate groups in the complex sphere of the chrome and a decrease of the charge of the chrome complex.

Recovery of Protein from Lime Liquors of Tanneries. By N. N. Oreshkov. *Legkaya Prom.* **9,** No. 1, 18 (1949). Through *C. A.* **46,** 2832 (1952). Protein suitable as a substitute for casein and rosin in paper making and also in plastics was obtained by neutralizing the total alkalinity of lime liquors with sulfuric acid. At one chrome tannery, 39 kg. acid yielded 100 kg. air dry protein.

Component Parts of Tanning Extract. By M. I. Karpman. *Legkaya Prom.* **9,** No. 1, 19 (1949). Through *C. A.* **46,** 2832 (1952). Analysis of dry and liquid oak, spruce and willow extracts indicates that upon evaporation to dryness, there is an increase in tannins and a decrease in nontannins.

New Raw Materials for Leather Substitutes. By I. U. Mishustin. *Legkaya Prom.* **9,** No. 1, 21 (1949). Through *C. A.* **46,** 2832 (1952). A review of developments outside the Soviet Union. 21 references.

Determination of Jelly Strength of Glues and Gelatins by the Boncher Jelly Tester. By W. S. Kaprowski (Union Glue and Gelatin Co., London). *Analyst* **76,** 733 (1951). Through *C. A.* **46,** 2833 (1952). A 5-mm. depression on the surface of the sample gel is produced by a hollow plunger 13 mm. in diameter. The force required to produce this depression is applied by adding water slowly. The volume of water used is measured.

The Tannins. By A. Deschamps. *Bull. assoc. anciens etud. brasseru* **47,** 165 (1951). Through *C. A.* **46,** 3783 (1952). A review with 55 references.

Bear Clover and Redwood as Tannin Possibilities. By E. Fretz. *J. Forestry* **46,** 688 (1948). Through *C. A.* **46,** 3783 (1952). *Chamaebatia foliolosa* contains, in its dried aereal shoots, 13.2 per cent tannin. Redwood *(Sequoia sempervirens)* gave 4.8 per cent of tannin in oven dried heartwood.

Use of Hexametaphosphate for Preventing Formation of Calcium Oxalate Scale During Manufacture of Solid Wattle Bark Extract. By D. M. Rice. *Proc. S. African Sugar Technol. Assoc.* 25, 68 (1951). Through *C. A.* **46,** 3783 (1952). Precipitation of calcium oxalate is prevented by the addition of 0.5-1.0 pound of $Na_6P_6O_{18}$ per ton of extract made depending on the Ca content of the water used.

Paper Chromatography of the Pyrogallol Tannins. By R. S. Asquith (Univ. Leeds, England). *Nature* **168,** 738 (1951). Through *C. A.* **46,** 3462 (1952). Two new solvents, phenol-acetic acid - water and phenol-chloracetic acid - water, are used to separate mixtures of complex phenols into well defined spots. The R_f values of the different tannins vary considerably with temperature. Chebulinic acid and its hydrolysis products, digalloyl glucose, split acid, and gallic acid can be separated by this method.

A Study of Vegetable Tanning Under the Conditions Used in the Argentine Republic. Influence of pH on Tanning with Sulfited Quebracho Extract. By H. Giovambattista, A. A. Giacomi and W. O. Palavecino. *Lab. ensayo Materiales e invest. technol.*, LaPlata, *Rep. Agr. Ser.* **2,** No. 37, 5 (1950). Through *C. A.* **46,** 4260 (1952). Salted cattle hides cut into strips 20 cm. wide were soaked, unhaired, and bated by conventional methods. Pieces 20 x 40 cm. were tanned in drums, in solutions of commercial sulfited quebracho extract gradually increasing in concentration from 0.5°Be. (2 days) to 1° (third day), 2° (4th day), 3-7° (5th to 7th day), 8° (8th to 11th day), and to 15°Be. for 20-24 hours. Some pieces were tanned at the natural pH (6.6-7.3; 5.5 in concentrated solutions), other with the natural pH of the quebracho extract and then by lowering it by 0.5 each day to 3.5, as the tanning advanced, by addition of lactic acid; still others were tanned starting with a pH of 5-5.5 and lowering it stepwise to 3.0. The tanned hides were then bleached in drums with 0.5-1.0 per cent $BaCl_2$, 0.5-1 per cent $MgSO_4$, and 0.5-1.0 per cent $NaHSO_3$, based on the weight of the hide. Leather was oiled with 1.0 per cent mineral oil and sulfated vegetable oil. In some experiments, $NaHSO_3$ was replaced with oxalic acid. The finished leathers were then oiled with mineral oil on the grain side. The leathers were conditioned at 65 per cent relative humidity at 20° and analyzed. The lactic acid treated leathers had lower pH and contained slightly less moisture, less ash, and less soluble matter, more combined tannin and leather substance and a greater degree of tanning (10-20 units) compared with leathers tanned at the natural pH. Where oxalic acid was used after tanning, the soluble matter was decreased and the combined tannin was increased.

Plastics from Quebracho Tannin. By R. Nico. *Lab. ensayo Materials e invest. technol., LaPlata, Rep. Ara. Ser.* **2,** No. 38, 5 (1950). Through *C. A.* **46,** 4267 (1952). Mixtures of 100 parts of powdered quebracho extract and 5-20 parts of powdered hexamethylenetetranine were molded into brittle, dark reddish brown, glossy objects at 130-65° by pressures of 50 kg. sq. cm. and up. By impregnating 100 parts of quebracho meals of varying degrees of fineness with aqueous solutions of 5-20 parts of hexamethylenetetranine, or of ammonia and formaldehyde, drying them, and molding them 2-10 minutes at 130-70° under pressures of 200-400 kg. sq. cm. (preferably after preliminary wetting with 5-10 per cent of alcohol) useful objects of good resistance to impact and to water were obtained. Glycerol or phthalates were suitable as plasticizers, and calcium stearate served as a mold lubricant. Satisfactory molding powders were made from wood flour, sawdust, or straw impregnated with solutions of quebracho extract and of hexamethylenetetramine. Other applications

were cloth and paper laminates, oil cloth, and adhesives (40-45 per cent neutral aqueous solutions which could be stored up to 10 days at 30° maximum, cured at 90-130° under 7-15 kg. sq. cm.

Lactic Acid in the Leather Industry. By U. Lubrano. *Cuoio, pelli mat. concianti*, **27,** 226 (1951). Through *C. A.* **46,** 4829 (1952). The results of deliming hides, limed with CaO and with CaO + Na_2S are tabulated. A solution of lactic acid equivalent to 2 per cent of the weight of the hide dissolved 58 per cent of the total CaO absorbed by the hide treated with CaO alone. Five per cent lactic acid removed 82 per cent of the CaO. The actual consumption of lactic acid is always greater than the amount calculated from the CaO content of the limed pelts, because some lactic acid combines with the protein.

The Problem of Hide Powder. By A. Gansser. *Cuoio, pelli. mat. concianti* **27,** 209 (1951). Through *C. A.* **46,** 4831 (1952). The various hide powders prepared for the determination of tannins by the shake method give different results, owing to the different structures of the material, as is shown, for example, by staining the hide powder with acid fuchsin. German hide powder gives the greatest absorption and French, American and English follow in that order. This is in accord with the decreasing pH values of the 4 types, which are respectively 6.60, 5.58, 5.56 and 5.25. To obtain a more uniform absorption of tannins in analysis, it is suggested that a mixture of the various kinds of hide powders be used. In this way the average differences in duplicate analyses, which may reach 0.42 per cent decrease to 0.04 per cent.

Turkish Valonias II. Various Grades of Valonia and Their Tannin Content. By O. Gerngross and E. Anseren. (Univ. Ankara, Turkey). *Communs. faculte sci. univ. Ankara* **3,** 87 (1950). Through *C. A.* **46,** 4831 (1952). In addition to 3 previously described types of valonia cups, 3 new types were collected in the Haci Kadin Valley near Ankara and in the Ege region. The same types of cups have a higher tannin content when grown in the Ege region, showing a climatic influence. Small, normally developed, mature crops frequently contain more tannin than the larger ones. The pH values of the aqueous extracts, containing 0.4 per cent tannin, of the 6 types are between 3.58 and 3.96 and do not show any characteristic differences. The inner layer of the cups contains up to 21.7 per cent less tannin than the scaleless outer layers, and the cup scales contain 6-7 per cent less tannin than the tip scales around the rim of the cups. The tip scales of a single cup have in general a higher density than the cup scales.

The Tannin of the Pods of Tara Cultivated in Italy. By G. A. Bravo. *Cuoio, pelli, mat. concianti*, **28,** 25 (1952). Through *C. A.* **46,** 4831 (1952). The pods of Tara from Sardinia gave, by the filter method, respectively for pods with and without seeds: tannin 42.6, 51.9; nontannins 17.8, 16.4 per cent. Liquid and solid extracts of tara gave, respectively: tannin 31.1, 68.0; nontannins 13.2, 28.5; insolubles 0.7, 2.3 per cent; tintometer readings: red 0.4, 0.5 and yellow 1.6, 2.9; pH 3.6, 3.85. The results of dyeing and printing textiles with tara tannin and basic dyes are described.

Chamois Dressing and Kid Leather Tanning with Immergan. By E. Immendorfer. *Mitt. chem. Forsch. Inst. Ind. oster* **5,** 105 (1951). Through *C. A.* **46,** 4832 (1952). The mechanism of tanning with Immergan and practical results are explained.

Free Amino Groups of Collagen. By J. H. Bowes and J. A. Moss. (Brit. Lea. Mfg. Research Assoc. Egham, Engl.). *Nature* **168,** 514 (1951). Through *C. A.* **46,** 4832 (1952). After heating ox hide collagen in water at 70°, and treating with alkali or urea, a small number of α-amino groups were detected by the reaction with dinitrofluorobenzene. The groups detected were aspartic acid, glutamic acid, glycine and phenylalanine. Proline could not be detected by this technique. This indicates either that (1) the molecular weight of collagen is greater than 1,500,000, (2) the molecule has a cyclic structure, or (3) the end group is inaccessible to dinitrofluorobenzene or is masked in some way by combination with some other group or with carbohydrate. Less dinitrophenylysine was isolated from the modified collagen than the amounts corresponding to their lysine contents. Heat denaturation of collagen causes shrinkage and probably involves folding of the chains, which may decrease the availability of the amino groups.

Preparation of Glue from Fish Wastes. By P. M. Chekalin. *Rybnoe Khoz.* **27,** No. 3, 24 (1951). Through *C. A.* **46,** 4832 (1952). The middle layer of the waste products of fish packing is treated with 2-3 per cent naphthalenesulfonic acids, the precipitate is washed with water at 60-70°, and the molten glue is shaped and cooled. After the first 4-5 days of storage some water separation may be observed. The glue is insoluble in cold water but is soluble in dilute $NaHCO_3$ or Na_2CO_3 and in 3-4 per cent lime water. It is best used in aqueous solution at 60-70°.

Preservation of Sheepskins with Brine. By I. Leontev. *Myasnaya Ind. S.S.S.R.,* **23,** No. 1, 12 (1952). Through *C. A.* **46,** 5347 (1952). The equipment and method are described for treating sheep and goat skins with brine followed by salting with fine salt. A small amount of sodium fluorosilicate is added to the brine, and either the fluorosilicate or p-dichlorobenzol is added to the salt.

Effect of Tanning on the Mechanical Properties of Leather. By G. I. Kutyanin. *Kolloid Zhur.* **14,** 46 (1952). Through *C. A.* **46,** 5347 (1952). The strength of leather is maximum at a moderate degree of tanning because moderate tanning causes formation of cross linkages between the protein chains without reducing the ability of the chains to be orientated by stress, while this ability is lowered by too many cross linkages. Rawhide shows a maximum of strength at a medium moisture content (26 parts of water per 100 parts dry hide) because water weakens the bond between the collagen chains but facilitates their orientation. The strength of the leather increases with water content because water does not weaken the cross linkages produced by tanning.

The Tannin of Eucalyptus Sideroxylon Bark. By P. Chambard, I. Jullien, and R. Lasserre. *Bull. assoc. franc. chim. inds. cuir* **9,** 162 (1951). Through *C. A.* **46,** 5349 (1952). Bleached and unbleached mixtures of a 20°Be. *E. sideroxylon* extract and 10, 20, and 30 per cent of a 20°Be. synthetic tannin extract (Albatan RS 4) were tested, viscosity decreased with increasing concentration of the syntan up to 20 per cent and was decreased by bleaching with sodium formate, bisulfite, and formic acid. Laboratory tests showed that penetration into the skin is more rapid and color of the leather is lighter when tanned with the extract in conjunction with the syntan. Additions of 20 per cent syntan gave the best results in respect to color and firmness of the leather. Skins tanned with bleached mixtures absorbed more tannin and contained more soluble matter.

Silica Tanning. Diffusion of Silica Sols Into Gelatin Gels. By P. Chambard and R. Lasserre. *Bull. assoc. fran. chim: mds. cuir* **10,** 179 (1951). Through *C. A.* **46,** 5349 (1952). Previous tests with silica-iron sols revealed that silica is fixed only in the outer layers of the skin. This has been further investigated. A 10 per cent gel was prepared from pure gelatin swollen in 0.2 *N* HCl solution at pH 1.5. Tanning tests were performed with a mixture of an acidified 10 per cent sodium silicate solution containing 29.7 per cent SiO_2 and 10.5 per cent Na_2O, and different amounts of an 8.7 per cent $Fe_2(SO_4)_3$ solution of zero basicity. Contraction of the gels was observed. A hard and thin layer was formed at the surface for which silica seemed to be responsible. Determination of the melting point of different layers of the tanned gels confirmed that silica tanned the surface layers only and completely, without penetration, owing to the large size of the SiO_2 aggregates. Iron salt tanned the inner layers of the gels weakly since the tanning solution was very acid. The tanning effect of Fe salt increased with its concentration. No silica-iron complex is formed since the proportion of Fe and SiO_2 absorbed differs from the proportion of these compounds in the original tanning liquor.

Silica Tanning. Silica-Collagen Combination. P. Chambard and R. Lasserre. *Bull. assoc. franc. chim. inds. cuir.* **10,** 187 (1951). Through *C. A.* **46,** 5350 (1952). The nature of fixation of SiO_2 from an acidified Na silicate solution with collagen has been investigated. It is believed that SiO_2 combines with the free amino groups of the skin through electrovalences and also through a coordination reaction with NH since there is considerable fixation of SiO_2 which decreased when the skin is deaminated. The possibility of a subsequent chrome tanning supports this hypothesis.

The Effects of Anionic Detergents on Collagens of Mammals and Teleostei. By K. H. Gustavson. Garverinaringens Forskningsinst, Stockholm). *Acta Chem. Scand.* **4,** 1171 (1950). Through *C. A.* **46,** 1953 (1952). From data on fixation of Cr by collagen it is shown that pretreatment of collagen with 10 per cent solutions of Na do-decyl sulfate causes permanent changes of the collagen which involve the coordinate rather than electrovalent bonds.

Colorimetric Method for Determining Oxygen Dissolved in Water Without Using Iodine Compounds. By G. Gad and A. Becker. *Gesundheitsing.* **69,** 358 (1948). Through *Sew. and Ind. Wastes,* **24,** 921 (1952). In a colorimetric method for determining dissolved oxygen, manganous chloride and sodium hydroxide are first added. The precipitate of manganous hydroxide is dissolved in dilute sulfuric acid and sodium pyrophosphate. An acid manganic phosphate, equivalent in amount to the dissolved oxygen and red-violet in color, is formed. The amount of oxygen present is calculated by comparison with a potassium permangante solution of known concentration. J. F. W.

A Critical Review of the Literature of 1951 on Sewage, Waste Treatment, and Water Pollution. By W. Rudolfs, et al. *Sew. and Ind. Wastes,* **24,** 541 (1952). This comprehensive review of the 1951 literature has been compiled by the Committee on Research, Section A, Federation of Sewage and Industrial Wastes Associations. It is presented under five headings: Analytical Methods (52 References); Sewage (201 References); Industrial Wastes (164 References); Radioactivity (94 References); and Water Pollution (256 References). J. F. W.

PATENTS

Leather Finishing. U. S. Pat. 2,593,108. A. F. R. Cotton, Merrick, N. Y. Appl. July 3, 1947. A leather finishing process including applying heat to at least one side of leather, with heat hot enough to materially contract the leather and with the leather permitted to contract and with the leather contacted by a moisture absorbent bed.

Process for the Production of High Purity Tanning Extracts. U. S. Pat. 2,594,291. T. C. Cordon, Erdenheim, Pa., and L. J. Wickerham, Peoria, Ill., assignors to U. S. A. Appl. Jan. 13, 1950. In a process for recovering tannins from canaigre by extracting canaigre roots with an aqueous extractant to produce a tannin-containing canaigre water-extract liquor and an extraction residue consisting of spent canaigre root material, the steps comprising: contacting the spent root material with an aqueous solution of a strong mineral acid at a temperature and for a length of time sufficient to cause hydrolysis of the starch present in said material; separating and neutralizing the resultant liquid hydrolyzate; inoculating the hydrolyzate with a yeast and allowing the fermentation to proceed until the major portion of the sugar content of the hydrolyzate has been consumed; separating the yeast cells from the fermented hydrolyzate and transferring them to the canaigre extract liquor; allowing the fermentation of the liquor to proceed substantially to completion and thereafter separating the yeast cells and recovering the alcohol from the fermented extract liquor.

Preparation of Collagenous Materials. U. S. Pat. 2,598,608. T. P. Salo, Cambridge, and D. F. Waugh, Belmont, Mass., assignors by mesne assignments to Research Corp., N. Y. Appl. June 11, 1946. In the process of converting a swollen mass of tendon pieces to a gel of solvated fibrils of substantially pure collagen from which filaments may be spun, the steps which comprise blending the swollen mass with a water to form a dilute sol and centrifuging the dilute sol prior to conversion to a gel for spinning.

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Na_2S	61.00

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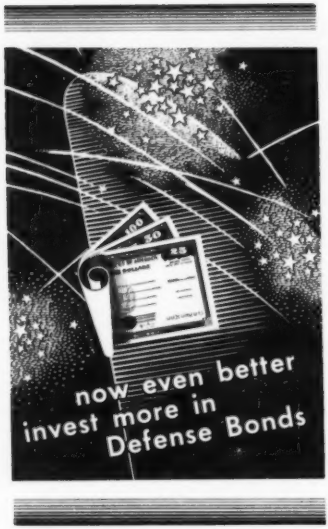

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